# Supporting Information

## 1-D "Platinum Wire" Stacking Structure Built of Platinum(II) Diimine Bis(σ-acetylide) Units with Luminescence in the NIR Region

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# Contents

**Table S1.** Crystal data and structure refinement for **1**·DMSO, **1**·1/2($CH_3CN$) and **1**·1/8($CH_2Cl_2$).

| | **1**·DMSO | **1**·1/2$CH_3CN$ | **1**·1/8($CH_2Cl_2$) |
|---|---|---|---|
| Empirical formula | $C_{32}H_{30}Br_2N_2OPtS$ | $C_{62}H_{51}Br_4N_5Pt$ | $C_{241}H_{194}Br_{16}Cl_2N_{16}Pt_8$ |
| *M* | 845.52 | 1575.90 | 6224.30 |
| Crystal system | triclinic | triclinic | monoclinic |
| Space group | *P-1* | *P-1* | *C2/c* |
| *a* / Å | 10.6084(7) | 8.9811(4) | 22.200(12) |
| *b* / Å | 12.8660(8) | 15.4169(8) | 21.156(12) |
| *c* / Å | 13.3514(9) | 20.7934(11) | 13.262(7) |
| α / ° | 61.360(4) | 99.006(4) | 90 |
| *β* / ° | 76.813(5) | 95.653(3) | 96.522(6) |
| *γ* / ° | 83.798(5) | 98.947(3) | 90 |
| *V* / Å$^3$ | 1557.17(18) | 2786.6(2) | 6188(6) |
| *Z* | 2 | 2 | 1 |
| $D_c$ /g·cm$^{-3}$ | 1.803 | 1.878 | 1.670 |
| $\mu$(mm$^{-1}$) | 7.166 | 7.927 | 7.158 |
| Radiation ($\lambda$, Å) | 0.71073 | 0.71073 | 0.71073 |
| *T* / K | 296(2) | 296(2) | 296(2) |
| *F*(000) | 816 | 1508 | 2970 |
| $R_{int}$ | 0.030 | 0.032 | 0.039 |
| Reflections collected / uniques | 10723/5449 | 13825/9659 | 15210/5425 |
| Observed reflections ($I > 2\sigma(I)$) | 4645 | 7222 | 3077 |
| $R1^a(I > 2\sigma(I))$ | 0.0325 | 0.0540 | 0.0425 |
| $wR2^b$(all data) | 0.0775 | 0.1547 | 0.1319 |
| GOF | 1.017 | 1.029 | 1.067 |

$^aR1 = \Sigma|F_o-F_c|/\Sigma F_o$, $^bwR2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)]^{1/2}$

**Table S2.** Selected bond lengths (Å), bond angles (º) and the shortest Pt···Pt (Å) distance for **1**·DMSO, **1**·1/2($CH_3CN$) and **1**·1/8($CH_2Cl_2$).

| | **1**·DMSO | **1**·1/2($CH_3CN$) | | **1**·1/8($CH_2Cl_2$) |
|---|---|---|---|---|
| Shortest Pt···Pt distance | 4.845 | 4.882 | | 3.341 |
| Pt-N | 2.074(5) | 2.0633(5) | 2.0459(6) | 2.061(7) |
| | 2.066(4) | 2.0482(7) | 2.0607(6) | 2.039(7) |
| Pt-C | 1.946(6) | 1.961(10) | 1.959(11) | 1.970(9) |
| | 1.959(7) | 1.9055(6) | 1.9797(7) | 1.946(10) |
| N-Pt-N | 78.89(17) | 79.02(3) | 79.25(3) | 79.4(3) |
| C-Pt-N | 94.4(2) | 94.5(3) | 94.5(3) | 96.4(4) |
| C-Pt-N | 95.9(2) | 95.26(3) | 97.58(3) | 95.3(3) |
| C-Pt-C | 90.8(2) | 91.9(4) | 88.00(3) | 88.9(4) |

**Table S3.** Hydrogen-bonding geometry (Å,°) and short interactions in **1**·DMSO, **1**·1/2($CH_3CN$) and **1**·1/8($CH_2Cl_2$).

**1**·DMSO

| *D*-H···*A* | *D*-H | H···*A* | *D*···*A* | *D*-H···*A* | Symmetry code |
|---|---|---|---|---|---|
| C4-H4···O1 | 0.93 | 2.38 | 3.249(9) | 156 | x, y, 1+z |
| C7-H7···O1 | 0.93 | 2.44 | 3.280(8) | 150 | x, y, 1+z |

| | center…center | Symmetry code |
|---|---|---|
| $\pi$(Cg1)···$\pi$(C11≡C12) | 3.455 | 2-x, 1-y, 2-z |

Cg1 is the pyridine ring containing N1 atom.

**1**·1/2($CH_3CN$)

| *D*-H···*A* | *D*-H | H···*A* | *D*···*A* | *D*-H···*A* | Symmetry code |
|---|---|---|---|---|---|
| C02-H02A···$\pi$(C11≡C12) | 0.96 | 2.76 | 3.598(14) | 146 | - |
| C4-H4···N01 | 0.93 | 2.69 | 3.606 | 170 | -x, -y, -z |
| C7-H7···N01 | 0.93 | 2.60 | 3.510(10) | 167 | -x, -y, -z |
| C20-H20A···Br3 | 0.96 | 2.81 | 3.577(12) | 137 | 2-x, 1-y, 1-z |
| C39-H39···N01 | 0.93 | 2.58 | 3.3350(12) | 138 | 1+x, y, z |
| C58-H58···Cg7 | 0.93 | 2.92 | 3.718 | 144 | - |

| | center…center | Symmetry code |
|---|---|---|
| $\pi$(Cg2)…$\pi$(Cg3) | 3.871 | -x, -y, -z |
| $\pi$(Cg3)…$\pi$(Cg4) | 3.718 | 1-x,-y,-z |
| $\pi$(Cg2)…$\pi$(C11≡C12) | 3.284 | 1-x,-y,-z |
| $\pi$(Cg5)…$\pi$(Cg6) | 3.497 | 2-x,1-y,1-z |
| $\pi$(Cg6)…$\pi$(Cg7) | 3.879 | 1-x,1-y,1-z |
| $\pi$(Cg5)…$\pi$(C41≡C42) | 3.599 | 1-x,1-y,1-z |

Cg2 is pyridine ring containing N1 atom, Cg3 is the pyridine ring containing N2 atom, Cg4 is the benzene ring containing C18 atom, Cg5 is pyridine ring containing N3 atom, Cg6 is pyridine ring containing N4 atom, Cg7 is the benzene ring containing C48 atom.

**1**·1/8($CH_2Cl_2$)

| | center…center | Symmetry code |
|---|---|---|
| $\pi$(Cg8)…$\pi$(C21≡C22) | 3.446 | -x,1-y,1-z |
| $\pi$(Cg9)…$\pi$(C11≡C12) | 3.420 | -x,1-y,1-z |

Cg8 is the pyridine ring containing N1 atom, Cg9 is the pyridine ring containing N2 atom.

**Table S4.** Partial molecular orbital compositions (%) in the ground state for **1** in dichloromethane solution from the TD-DFT calculation.

| orbital | energy (eV) | MO contribution (%) | | |
|---|---|---|---|---|
| | | Pt(s/p/d) | C≡CPh-Et-4 | DiBrbpy |
| LUMO+11 | 0.60 | 52.2(0/52/48) | 32.1 | 15.7 |
| LUMO+8 | -0.24 | 41.9(94/5/1) | 56.3 | 1.8 |
| LUMO+7 | -0.02 | 2.6(17/20/63) | 73.5 | 23.9 |
| LUMO+6 | -0.09 | 6.3(74/14/12) | 5.4 | 88.3 |
| LUMO+5 | -0.14 | 4.7(2/34/64) | 13.3 | 82.0 |
| LUMO+4 | -0.17 | 7.7(81/15/4) | 12.7 | 79.6 |
| LUMO+3 | -0.26 | 18.2(5/73/22) | 68.3 | 13.5 |
| LUMO+2 | -1.55 | 1.5(1/1/98) | 0.7 | 97.8 |
| LUMO+1 | -1.79 | 2.8(0/59/41) | 1.0 | 96.2 |
| LUMO | -2.76 | 4.4(0/36/64) | 2.6 | 93.0 |
| HOMO | -5.67 | 16.1(0/1/99) | 82.3 | 1.6 |
| HOMO-1 | -5.84 | 12.1(0/5/95) | 85.0 | 2.9 |
| HOMO-2 | -6.34 | 33.9(0/1/99) | 61.1 | 5.0 |
| HOMO-3 | -6.61 | 21.3(0/2/98) | 73.4 | 5.3 |
| HOMO-4 | -6.87 | 96.4(28/0/72) | 2.9 | 0.7 |
| HOMO-5 | -6.95 | 0.8(0/1/99) | 99.1 | 0.1 |
| HOMO-6 | -7.02 | 0.05(4/4/92) | 99.94 | 0.01 |
| HOMO-7 | -7.50 | 29.6(0/0/100) | 59.4 | 11.0 |
| HOMO-8 | -7.81 | 12.3(0/2/98) | 80.0 | 7.7 |
| HOMO-9 | -8.01 | 1.6(0/2/98) | 10.2 | 88.2 |
| HOMO-10 | -8.13 | 9.8(0/1/99) | 23.1 | 67.1 |

**Table S5.** Absorption and emission transition properties of **1** in dichloromethane solution by TD-DFT method at the PBE1PBE level with the polarized continuum model (PCM).

| States | *E*, nm (eV) | O.S. | Component | Contri. | Assignment | Measured Wavelength (nm) |
|---|---|---|---|---|---|---|
| $T_1$ | 591 (2.10) | 0.0000 | HOMO→LUMO | 91% | $^3$LLCT/$^3$MLCT | 640 |
| | | | HOMO-1→LUMO | 7% | $^3$LLCT/$^3$MLCT | |
| $S_2$ | 517 (2.40) | 0.0928 | HOMO-1→LUMO | 100% | $^1$LLCT/$^1$MLCT | |
| $S_3$ | 453 (2.73) | 0.1063 | HOMO-2→LUMO | 100% | $^1$LLCT/$^1$MLCT | 469 |
| $S_5$ | 405 (3.07) | 0.0672 | HOMO-3→LUMO | 100% | $^1$LLCT/$^1$MLCT | 429 |
| $S_8$ | 356 (3.49) | 0.1287 | HOMO→LUMO+2 | 71% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO+1 | 29% | $^1$LLCT/$^1$MLCT | |
| $S_9$ | 341 (3.63) | 0.0721 | HOMO-1→LUMO+2 | 100% | $^1$LLCT/$^1$MLCT | |
| $S_{19}$ | 283 (4.38) | 0.0695 | HOMO-8→LUMO | 96% | $^1$LLCT/$^1$MLCT | 291 |
| $S_{20}$ | 279 (4.45) | 0.6633 | HOMO-9→LUMO | 53% | $^1$IL/$^1$LLCT | |
| | | | HOMO-10→LUMO | 35% | $^1$IL/$^1$LLCT | |
| | | | HOMO-3→LUMO+2 | 9% | $^1$LLCT/$^1$MLCT | |
| $S_{21}$ | 272 (4.55) | 0.7132 | HOMO→LUMO+3 | 100% | $^1$IL/$^1$MC$^1$/LLCT | |
| $S_{24}$ | 262 (4.73) | 0.2656 | HOMO→LUMO+5 | 31% | $^1$IL/$^1$LLCT/$^1$MLCT | 265 |
| | | | HOMO→LUMO+11 | 21% | $^1$IL/$^1$MC/$^1$LLCT | |
| | | | HOMO-1→LUMO+3 | 19% | $^1$IL/$^1$MC/$^1$LLCT | |
| | | | HOMO→LUMO+4 | 11% | $^1$IL/$^1$LLCT/$^1$MLCT | |
| | | | HOMO→LUMO+6 | 11% | $^1$LLCT/$^1$MLCT | |
| $S_{26}$ | 260 (4.78) | 0.0773 | HOMO-1→LUMO+3 | 63% | $^1$IL/$^1$MC/$^1$LLCT | |
| | | | HOMO-2→LUMO+3 | 12% | $^1$IL/$^1$MC/$^1$LLCT | |
| | | | HOMO→LUMO+5 | 11% | $^1$IL/$^1$LLCT/$^1$MLCT | |
| $S_{30}$ | 252 (4.92) | 0.1779 | HOMO-5→LUMO+2 | 26% | $^1$LLCT | 241 |
| | | | HOMO-1→LUMO+5 | 20% | $^1$IL/$^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO+4 | 9% | $^1$IL/$^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO+11 | 8% | $^1$IL/$^1$MC/$^1$LLCT | |
| | | | HOMO-1→LUMO+7 | 7% | $^1$IL/$^1$LLCT/$^1$MLCT | |
| $S_{31}$ | 252 (4.92) | 0.1283 | HOMO-2→LUMO+3 | 29% | $^1$IL/$^1$MC/$^1$LLCT | |
| | | | HOMO-5→LUMO+2 | 13% | $^1$LLCT | |
| | | | HOMO-2→LUMO+7 | 11% | $^1$IL/$^1$LLCT/$^1$MLCT | |
| | | | HOMO→LUMO+6 | 11% | $^1$LLCT/$^1$MLCT | |

| | | | | | |
|---|---|---|---|---|---|
| $S_{32}$ | 249 | 0.0819 | HOMO-5→LUMO+2 | 36% | $^1$LLCT |
| | (4.99) | | HOMO→LUMO+8 | 17% | $^1$IL/$^1$MC/$^1$LLCT |
| | | | HOMO-7→LUMO+1 | 13% | $^1$IL/$^1$LLCT/$^1$MLCT |
| $S_{36}$ | 246 | 0.1609 | HOMO→LUMO+7 | 26% | $^1$IL/$^1$LLCT/$^1$MLCT |
| | (5.05) | | HOMO-3→LUMO+3 | 12% | $^1$MC/$^1$IL/$^1$LLCT |
| | | | HOMO-1→LUMO+6 | 11% | $^1$LLCT/$^1$MLCT |
| | | | HOMO-6→LUMO+2 | 10% | $^1$LLCT |
| | | | HOMO-1→LUMO+4 | 8% | $^1$IL/$^1$LLCT/$^1$MLCT |
| | | | HOMO-1→LUMO+11 | 8% | $^1$IL/$^1$MC/$^1$LLCT |
| | | | HOMO→LUMO+8 | 8% | $^1$IL/$^1$MC/$^1$LLCT |

**Table S6.** Partial molecular orbital compositions (%) in the ground state for the two-molecule model of **1**·DMSO in the solid state by TD-DFT method at the PBE1PBE level.

| orbital | energy (eV) | MO contribution (%) | | |
|---|---|---|---|---|
| | | Pt(s/p/d) | C≡CPh-Et-4 | DiBrbpy |
| LUMO+5 | -1.29 | 2.85(21/52/27) | 0.65 | 96.50 |
| LUMO+4 | -1.37 | 3.57(41/49/10) | 1.18 | 95.25 |
| LUMO+3 | -1.63 | 2.85(4/59/37) | 1.38 | 95.77 |
| LUMO+2 | -1.71 | 4.61(41/45/14) | 2.54 | 92.85 |
| LUMO+1 | -2.54 | 3.89(7/28/65) | 2.69 | 93.42 |
| LUMO | -2.58 | 5.53(9/48/43) | 2.83 | 91.64 |
| HOMO | -5.35 | 14.10(2/2/96) | 84.43 | 1.47 |
| HOMO-1 | -5.37 | 13.38(0/2/98) | 85.13 | 1.49 |
| HOMO-2 | -5.58 | 15.04(0/5/95) | 81.64 | 3.32 |
| HOMO-3 | -5.59 | 15.00(0/5/95) | 80.96 | 4.04 |
| HOMO-4 | -5.95 | 32.96(1/1/98) | 61.58 | 5.46 |
| HOMO-5 | -5.99 | 30.40(1/3/96) | 64.28 | 5.32 |
| HOMO-6 | -6.29 | 22.97(6/3/91) | 70.95 | 6.08 |
| HOMO-7 | -6.31 | 19.50(1/3/96) | 76.69 | 3.81 |
| HOMO-8 | -6.54 | 86.65(28/0/72) | 7.12 | 6.23 |
| HOMO-9 | -6.59 | 89.10(27/0/73) | 3.62 | 7.28 |
| HOMO-14 | -7.31 | 27.67(0/1/99) | 61.52 | 10.81 |
| HOMO-15 | -7.34 | 27.50(1/0/99) | 60.82 | 11.68 |

**Table S7.** Absorption and emission transition properties for the two-molecule model of **1**·DMSO in the solid state by TD-DFT method at the PBE1PBE level.

| States | *E*, nm (eV) | O.S. | Component | Contri. | Assignment | Measured Wavelength (nm) |
|---|---|---|---|---|---|---|
| $T_1$ | 617 (2.01) | 0.0000 | HOMO→LUMO | 72% | $^3$LLCT/$^3$MLCT | 570 |
| | | | HOMO-1→LUMO+1 | 20% | $^3$LLCT/$^3$MLCT | |
| $T_2$ | 613 (2.02) | 0.0000 | HOMO-1→LUMO | 48% | $^3$LLCT/$^3$MLCT | |
| | | | HOMO→LUMO+1 | 45% | $^3$LLCT/$^3$MLCT | |
| $T_3$ | 581 (2.14) | 0.0000 | HOMO-1→LUMO | 35% | $^3$LLCT/$^3$MLCT | |
| | | | HOMO→LUMO+1 | 31% | $^3$LLCT/$^3$MLCT | |
| | | | HOMO-2→LUMO+1 | 18% | $^3$LLCT/$^3$MLCT | |
| | | | HOMO-3→LUMO | 15% | $^3$LLCT/$^3$MLCT | |
| $S_6$ | 529 (2.34) | 0.0446 | HOMO-3→LUMO | 84% | $^1$LLCT/$^1$MLCT | 501 |
| | | | HOMO-2→LUMO | 8% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO→LUMO+1 | 8% | $^1$LLCT/$^1$MLCT | |
| $S_8$ | 524 (2.37) | 0.0412 | HOMO-2→LUMO+1 | 81% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO→LUMO+1 | 9% | $^1$LLCT/$^1$MLCT | |
| $S_{10}$ | 475 (2.61) | 0.1298 | HOMO-4→LUMO | 71% | $^1$LLCT/$^1$MLCT | 462 |
| | | | HOMO-5→LUMO+1 | 21% | $^1$LLCT/$^1$MLCT | |
| $S_{16}$ | 418 (2.96) | 0.0380 | HOMO-7→LUMO | 70% | $^1$LLCT/$^1$MLCT | 412 |
| | | | HOMO-6→LUMO+1 | 12% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO+2 | 12% | $^1$LLCT/$^1$MLCT | |
| $S_{24}$ | 383 (3.24) | 0.0338 | HOMO-3→LUMO+2 | 61% | $^1$LLCT/$^1$MLCT | 385 |
| | | | HOMO→LUMO+3 | 16% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO+2 | 7% | $^1$LLCT/$^1$MLCT | |
| $S_{27}$ | 377 (3.29) | 0.0582 | HOMO-9→LUMO | 36% | $^1$MLCT | |
| | | | HOMO-8→LUMO+1 | 33% | $^1$MLCT | |
| | | | HOMO-2→LUMO+3 | 14% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO+4 | 11% | $^1$LLCT/$^1$MLCT | |
| $S_{31}$ | 363 (3.41) | 0.0500 | HOMO→LUMO+5 | 41% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO+4 | 24% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-4→LUMO+2 | 18% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-2→LUMO+3 | 9% | $^1$LLCT/$^1$MLCT | |
| $S_{33}$ | 358 (3.46) | 0.0477 | HOMO-4→LUMO+2 | 56% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-5→LUMO+3 | 18% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-2→LUMO+3 | 10% | $^1$LLCT/$^1$MLCT | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | HOMO→LUMO+5 | 8% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO+4 | 8% | $^1$LLCT/$^1$MLCT | |
| $S_{38}$ | 344 (3.60) | 0.0422 | HOMO-2→LUMO+5 | 83% | $^1$LLCT/$^1$MLCT | 344 |
| | | | HOMO-3→LUMO+4 | 9% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO→LUMO+5 | 8% | $^1$LLCT/$^1$MLCT | |
| $S_{49}$ | 321 (3.87) | 0.0348 | HOMO-4→LUMO+4 | 36% | $^1$LLCT/$^1$MLCT | 315 |
| | | | HOMO-7→LUMO+2 | 36% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-6→LUMO+3 | 10% | $^1$LLCT/$^1$MLCT | |
| $S_{56}$ | 313 (3.96) | 0.0392 | HOMO-5→LUMO+5 | 76% | $^1$LLCT/$^1$MLCT | |
| $S_{59}$ | 307 (4.04) | 0.0349 | HOMO-14→LUMO | 71% | $^1$IL/$^1$LLCT/$^1$MLCT | 300 |
| | | | HOMO-15→LUMO+1 | 9% | $^1$IL/$^1$LLCT/$^1$MLCT | |

**Table S8.** Partial molecular orbital compositions (%) in the ground state for the two-molecule model of **1**·1/2($CH_3CN$) in the solid state by TD-DFT method at the PBE1PBE level.

| orbital | energy (eV) | MO contribution (%) | | |
|---|---|---|---|---|
| | | Pt(s/p/d) | C≡CPh-Et-4 | DiBrbpy |
| LUMO+5 | -1.41 | 2.86(48/24/28) | 1.89 | 95.25 |
| LUMO+4 | -1.44 | 3.16(29/56/15) | 2.72 | 94.12 |
| LUMO+3 | -1.70 | 2.17(5/50/45) | 0.44 | 97.39 |
| LUMO+2 | -1.73 | 2.71(27/52/21) | 2.81 | 94.48 |
| LUMO+1 | -2.51 | 4.78(5/22/73) | 4.67 | 90.55 |
| LUMO | -2.59 | 5.60(6/41/53) | 4.31 | 90.09 |
| HOMO | -5.26 | 17.01(1/1/98) | 79.72 | 3.27 |
| HOMO-1 | -5.29 | 16.92(1/1/98) | 80.88 | 2.20 |
| HOMO-2 | -5.46 | 18.06(1/8/91) | 75.79 | 6.15 |
| HOMO-3 | -5.48 | 17.91(0/9/91) | 74.67 | 7.42 |
| HOMO-12 | -6.94 | 10.39(10/8/82) | 82.02 | 7.59 |
| HOMO-13 | -6.97 | 6.17(5/4/91) | 87.88 | 5.95 |
| HOMO-14 | -7.03 | 34.77(0/0/100) | 49.72 | 15.51 |
| HOMO-15 | -7.04 | 37.77(0/0/100) | 45.76 | 16.47 |
| HOMO-16 | -7.16 | 23.54(3/1/96) | 64.55 | 11.91 |

**Table S9.** Absorption and emission transition properties for the two-molecule model of **1**·1/2($CH_3CN$) in the solid state by TD-DFT method at the PBE1PBE level.

| States | *E*, nm (eV) | O.S. | Component | Contri. | Assignment | Measured Wavelength (nm) |
|---|---|---|---|---|---|---|
| $T_1$ | 683 (1.82) | 0.0000 | HOMO→LUMO | 78% | $^3$LLCT/$^3$MLCT | 625 |
| | | | HOMO-1→LUMO+1 | 15% | $^3$LLCT/$^3$MLCT | |
| $T_2$ | 674 (1.84) | 0.0000 | HOMO-1→LUMO | 50% | $^3$LLCT/$^3$MLCT | |
| | | | HOMO→LUMO+1 | 40% | $^3$LLCT/$^3$MLCT | |
| | | | HOMO-3→LUMO | 7% | $^3$LLCT/$^3$MLCT | |
| $T_3$ | 624 (1.99) | 0.0000 | HOMO→LUMO+1 | 45% | $^3$LLCT/$^3$MLCT | |
| | | | HOMO-1→LUMO | 43% | $^3$LLCT/$^3$MLCT | |
| | | | HOMO-2→LUMO+1 | 12% | $^3$LLCT/$^3$MLCT | |
| $S_2$ | 618 (2.00) | 0.0365 | HOMO-1→LUMO | 85% | $^1$LLCT/$^1$MLCT | 582 |
| $S_3$ | 602 (2.06) | 0.0591 | HOMO→LUMO+1 | 88% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO | 8% | $^1$LLCT/$^1$MLCT | |
| $S_6$ | 532 (2.33) | 0.1883 | HOMO-3→LUMO | 92% | $^1$LLCT/$^1$MLCT | 530 |
| $S_8$ | 521 (2.38) | 0.1427 | HOMO-2→LUMO+1 | 96% | $^1$LLCT/$^1$MLCT | |
| $S_{17}$ | 424 (2.93) | 0.0576 | HOMO→LUMO+3 | 79% | $^1$LLCT/$^1$MLCT | 430 |
| | | | HOMO-1→LUMO+2 | 17% | $^1$LLCT/$^1$MLCT | |
| $S_{26}$ | 388 (3.19) | 0.1123 | HOMO-1→LUMO+4 | 48% | $^1$LLCT/$^1$MLCT | 390 |
| | | | HOMO-3→LUMO+2 | 27% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO→LUMO+5 | 15% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-2→LUMO+5 | 7% | $^1$LLCT/$^1$MLCT | |
| $S_{28}$ | 384 (3.23) | 0.0346 | HOMO-2→LUMO+3 | 47% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-3→LUMO+4 | 20% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-3→LUMO+2 | 13% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO+4 | 8% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO+2 | 7% | $^1$LLCT/$^1$MLCT | |
| $S_{36}$ | 361 (3.43) | 0.1556 | HOMO-3→LUMO+4 | 45% | $^1$LLCT/$^1$MLCT | 346 |
| | | | HOMO-2→LUMO+5 | 36% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-1→LUMO+4 | 9% | $^1$LLCT/$^1$MLCT | |
| $S_{42}$ | 346 (3.59) | 0.0396 | HOMO-13→LUMO | 58% | $^1$LLCT | |
| | | | HOMO-12→LUMO+1 | 42% | $^1$LLCT/$^1$MLCT | |
| $S_{53}$ | 322 (3.85) | 0.0675 | HOMO-16→LUMO | 54% | $^1$IL/$^1$LLCT/$^1$MLCT | 323 |
| | | | HOMO-13→LUMO | 15% | $^1$LLCT | |
| | | | HOMO-12→LUMO+1 | 9% | $^1$LLCT/$^1$MLCT | |
| | | | HOMO-15→LUMO | 9% | $^1$IL/$^1$LLCT/$^1$MLCT | |
| | | | HOMO-14→LUMO+1 | 7% | $^1$IL/$^1$LLCT/$^1$MLCT | |

**Table S10.** Partial molecular orbital compositions (%) in the ground state for the two-molecule model of **1**·1/8($CH_2Cl_2$) in the solid state by TD-DFT method at the PBE1PBE level.

| orbital | energy (eV) | MO contribution (%) | | |
|---|---|---|---|---|
| | | Pt(s/p/d) | C≡C$C_6H_4$Et-4 | DiBrbpy |
| LUMO+5 | -1.29 | 2.35(3/81/16) | 0.06 | 97.59 |
| LUMO+4 | -1.30 | 2.57(50/12/38) | 2.48 | 94.95 |
| LUMO+3 | -1.43 | 3.19(81/9/10) | 1.20 | 95.61 |
| LUMO+2 | -1.63 | 4.51(25/57/18) | 1.11 | 94.38 |
| LUMO+1 | -2.41 | 3.71(39/15/46) | 2.88 | 93.41 |
| LUMO | -2.51 | 6.91(9/41/50) | 4.30 | 88.79 |
| HOMO | -5.25 | 19.85(0/6/94) | 77.89 | 2.26 |
| HOMO-1 | -5.37 | 43.53(21/1/78) | 53.48 | 2.99 |
| HOMO-2 | -5.39 | 16.44(2/1/97) | 81.46 | 2.10 |
| HOMO-3 | -5.48 | 21.29(2/8/90) | 71.81 | 6.90 |
| HOMO-4 | -5.86 | 63.36(23/3/74) | 31.95 | 4.69 |
| HOMO-9 | -6.69 | 1.78(0/10/90) | 96.67 | 1.55 |
| HOMO-10 | -6.70 | 1.85(4/5/91) | 96.30 | 1.85 |
| HOMO-11 | -6.71 | 5.47(1/1/98) | 90.17 | 4.36 |
| HOMO-12 | -6.74 | 3.49(6/6/88) | 95.73 | 0.78 |
| HOMO-13 | -7.06 | 33.09(0/0/100) | 45.71 | 21.20 |
| HOMO-14 | -7.10 | 30.04(2/1/97) | 50.88 | 19.08 |
| HOMO-15 | -7.13 | 53.62(13/0/87) | 41.60 | 4.78 |
| HOMO-16 | -7.15 | 48.90(13/1/86) | 48.14 | 2.96 |
| HOMO-17 | -7.26 | 64.47(20/0/80) | 23.60 | 11.93 |

**Table S11.** Absorption and emission transition properties for the two-molecule model of **1**·1/8($CH_2Cl_2$) in the solid state by TD-DFT method at the PBE1PBE level.

| States | *E*, nm (eV) | O.S. | Component | Contri. | Assignment | Measured Wavelength (nm) |
|---|---|---|---|---|---|---|
| $T_1$ | 655 (1.89) | 0.0000 | HOMO→LUMO | 100% | $^3$MMLCT/$^3$LLCT | 1022 |
| $S_1$ | 623 (1.99) | 0.0000 | HOMO→LUMO | 100% | $^1$MLCT/$^1$LLCT | 761 |
| $S_2$ | 612 (2.02) | 0.0250 | HOMO-1→LUMO | 87% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-4→LUMO | 8% | $^1$MLCT/$^1$LLCT | |
| $S_5$ | 573 (2.17) | 0.0637 | HOMO-2→LUMO | 88% | $^1$MLCT/$^1$LLCT | 670 |
| | | | HOMO→LUMO+1 | 9% | $^1$MLCT/$^1$LLCT | |
| $S_8$ | 521 (2.38) | 0.0985 | HOMO-3→LUMO+1 | 91% | $^1$MLCT/$^1$LLCT | 534 |
| | | | HOMO-4→LUMO | 9% | $^1$MLCT/$^1$LLCT | |
| $S_9$ | 487 (2.55) | 0.1741 | HOMO-4→LUMO | 84% | $^1$MLCT/$^1$LLCT | 494 |
| | | | HOMO-1→LUMO | 11% | $^1$MLCT/$^1$LLCT | |
| $S_{19}$ | 398 (3.12) | 0.0239 | HOMO→LUMO+3 | 73% | $^1$MLCT/$^1$LLCT | 423 |
| | | | HOMO-2→LUMO+2 | 22% | $^1$MLCT/$^1$LLCT | |
| $S_{24}$ | 384 (3.23) | 0.0508 | HOMO→LUMO+4 | 62% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-1→LUMO+5 | 21% | $^1$MLCT/$^1$LLCT | |
| $S_{30}$ | 374 (3.32) | 0.0323 | HOMO-1→LUMO+5 | 41% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-3→LUMO+3 | 27% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO→LUMO+4 | 24% | $^1$MLCT/$^1$LLCT | |
| $S_{32}$ | 361 (3.43) | 0.0586 | HOMO-3→LUMO+4 | 36% | $^1$MLCT/$^1$LLCT | 356 |
| | | | HOMO-2→LUMO+5 | 28% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-3→LUMO+3 | 18% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-4→LUMO+2 | 16% | $^1$MLCT/$^1$LLCT | |
| $S_{33}$ | 358.09 (3.46) | 0.0995 | HOMO-4→LUMO+2 | 76% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-2→LUMO+5 | 7% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO→LUMO+4 | 7% | $^1$MLCT/$^1$LLCT | |
| $S_{35}$ | 354 (3.50) | 0.0858 | HOMO-3→LUMO+4 | 55% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-2→LUMO+5 | 33% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-3→LUMO+3 | 7% | $^1$MLCT/$^1$LLCT | |
| $S_{39}$ | 344 (3.61) | 0.0358 | HOMO-11→LUMO | 74% | $^1$LLCT | |
| | | | HOMO-10→LUMO | 11% | $^1$LLCT | |
| | | | HOMO-13→LUMO | 8% | $^1$IL/$^1$LLCT/$^1$MLCT | |
| $S_{48}$ | 328 (3.78) | 0.0209 | HOMO-4→LUMO+5 | 80% | $^1$MLCT/$^1$LLCT | 310 |
| | | | HOMO-9→LUMO+1 | 13% | $^1$LLCT | |
| $S_{52}$ | 325 (3.82) | 0.0203 | HOMO-17→LUMO+1 | 30% | $^1$IL/$^1$LLCT/$^1$MLCT | |
| | | | HOMO-15→LUMO+1 | 25% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-16→LUMO+1 | 22% | $^1$MLCT/$^1$LLCT | |

| | | | | | |
|---|---|---|---|---|---|
| | | | HOMO-13→LUMO | 10% | $^1$IL/$^1$LLCT/$^1$MLCT |
| $S_{53}$ | 321 (3.86) | 0.0228 | HOMO-13→LUMO | 44% | $^1$IL/$^1$LLCT/$^1$MLCT |
| | | | HOMO-12→LUMO+1 | 29% | $^1$LLCT |
| | | | HOMO-11→LUMO | 13% | $^1$LLCT |
| | | | HOMO-14→LUMO | 12% | $^1$IL/$^1$LLCT/$^1$MLCT |
| $S_{60}$ | 313 (3.96) | 0.0465 | HOMO-14→LUMO | 86% | $^1$IL/$^1$LLCT/$^1$MLCT |

**Table S12.** Partial molecular orbital compositions (%) in the ground state for the three-molecule model of **1**·1/8($CH_2Cl_2$) in the solid state by TD-DFT method at the PBE1PBE level.

| orbital | energy (eV) | MO contribution (%) | | |
|---|---|---|---|---|
| | | Pt(s/p/d) | C≡CPh-Et-4 | DiBrbpy |
| LUMO+7 | -1.15 | 4.36(24/50/26) | 1.99 | 93.65 |
| LUMO+6 | -1.29 | 2.78(16/79/5) | 1.43 | 95.79 |
| LUMO+5 | -1.32 | 2.45(9/77/14) | 1.83 | 95.72 |
| LUMO+4 | -1.53 | 4.38(55/38/7) | 1.29 | 94.33 |
| LUMO+3 | -1.59 | 4.28(7/91/2) | 43.87 | 51.85 |
| LUMO+2 | -2.07 | 4.31(19/37/44) | 4.25 | 91.44 |
| LUMO+1 | -2.45 | 5.22(75/18/7) | 4.54 | 90.24 |
| LUMO | -2.54 | 6.70(42/49/9) | 4.53 | 88.77 |
| HOMO | -5.16 | 54.74(31/0/69) | 42.55 | 2.71 |
| HOMO-1 | -5.18 | 19.09(3/9/88) | 78.59 | 2.32 |
| HOMO-2 | -5.23 | 24.54(21/8/71) | 72.97 | 2.49 |
| HOMO-3 | -5.40 | 22.50(6/5/89) | 70.76 | 6.74 |
| HOMO-4 | -5.45 | 18.65(1/2/97) | 77.73 | 3.62 |
| HOMO-5 | -5.59 | 42.24(24/3/73) | 50.86 | 6.90 |
| HOMO-6 | -5.61 | 33.81(4/3/93) | 60.90 | 5.29 |

**Table S13.** Absorption and emission transition properties for the three-molecule model of **1**·1/8($CH_2Cl_2$) in the solid state by TD-DFT method at the PBE1PBE level.

| States | *E*, nm (eV) | O.S. | Component | Contri. | Assignment | Measured Wavelength (nm) |
|---|---|---|---|---|---|---|
| $T_1$ | 707 (1.75) | 0.0000 | HOMO→LUMO | 94% | $^3$MMLCT/$^3$LLCT | 1022 |
| $S_1$ | 666 (1.86) | 0.0271 | HOMO→LUMO | 84% | $^1$MLCT/$^1$LLCT | 761 |
| | | | HOMO-2→LUMO | 9% | $^1$MLCT/$^1$LLCT | |
| $S_2$ | 641 (1.93) | 0.0152 | HOMO→LUMO+1 | 79% | $^1$MLCT/$^1$LLCT | 670 |
| | | | HOMO-2→LUMO+1 | 8% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-5→LUMO+1 | 7% | $^1$MLCT/$^1$LLCT | |
| $S_3$ | 631 (1.96) | 0.0263 | HOMO-2→LUMO | 50% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-1→LUMO | 37% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO→LUMO | 7% | $^1$MLCT/$^1$LLCT | |
| $S_6$ | 563 (2.20) | 0.0321 | HOMO-3→LUMO | 36% | $^1$MLCT/$^1$LLCT | 534 |
| | | | HOMO-4→LUMO+1 | 18% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-4→LUMO | 13% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-3→LUMO+1 | 10% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-2→LUMO+1 | 8% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-6→LUMO | 8% | $^1$MLCT/$^1$LLCT | |
| $S_{10}$ | 536 (2.31) | 0.0331 | HOMO-3→LUMO+1 | 45% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-2→LUMO+1 | 22% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-5→LUMO | 13% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-5→LUMO+1 | 10% | $^1$MLCT/$^1$LLCT | |
| $S_{12}$ | 525 (2.36) | 0.0578 | HOMO-6→LUMO | 49% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-5→LUMO | 16% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-3→LUMO | 14% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-4→LUMO | 10% | $^1$MLCT/$^1$LLCT | |
| $S_{16}$ | 499 (2.48) | 0.0736 | HOMO-6→LUMO+1 | 54% | $^1$MLCT/$^1$LLCT | 494 |
| | | | HOMO-5→LUMO | 14% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-3→LUMO+1 | 11% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-5→LUMO+1 | 8% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-2→LUMO+2 | 8% | $^1$MLCT/$^1$LLCT | |
| $S_{19}$ | 479 (2.60) | 0.0249 | HOMO-5→LUMO+1 | 53% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-3→LUMO+1 | 19% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-4→LUMO+1 | 11% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-3→LUMO+2 | 9% | $^1$MLCT/$^1$LLCT | |
| $S_{20}$ | 467 (2.66) | 0.0305 | HOMO-3→LUMO+2 | 78% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-4→LUMO+2 | 15% | $^1$MLCT/$^1$LLCT | |
| $S_{24}$ | 440 (2.82) | 0.0626 | HOMO-6→LUMO+2 | 88% | $^1$MLCT/$^1$LLCT | 423 |
| | | | HOMO-5→LUMO+2 | 9% | $^1$MLCT/$^1$LLCT | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | $^1$MLCT/$^1$LLCT | |
| $S_{45}$ | 385 (3.22) | 0.0205 | HOMO-1→LUMO+6 | 21% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-4→LUMO+3 | 18% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-5→LUMO+3 | 13% | $^1$IL/$^1$MLCT/$^1$LLCT | |
| | | | HOMO-3→LUMO+4 | 10% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-6→LUMO+3 | 9% | $^1$IL/$^1$MLCT/$^1$LLCT | |
| | | | HOMO-1→LUMO+7 | 8% | $^1$MLCT/$^1$LLCT | |
| $S_{47}$ | 384 (3.23) | 0.0233 | HOMO-2→LUMO+5 | 26% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-1→LUMO+5 | 26% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-3→LUMO+4 | 13% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-6→LUMO+3 | 13% | $^1$IL/$^1$LLCT/$^1$MLCT | |
| $S_{52}$ | 375 (3.31) | 0.0549 | HOMO-6→LUMO+3 | 47% | $^1$IL/$^1$LLCT/$^1$MLCT | 356 |
| | | | HOMO-5→LUMO+3 | 16% | $^1$IL/$^1$LLCT/$^1$MLCT | |
| | | | HOMO-2→LUMO+5 | 8% | $^1$MLCT/$^1$LLCT | |
| | | | HOMO-4→LUMO+3 | 8% | $^1$IL/$^1$LLCT/$^1$MLCT | |

**Table S14.** Partial molecular orbital compositions (%) in the ground state for the four-molecule model of **1**·1/8($CH_2Cl_2$) in the solid state by TD-DFT method at the PBE1PBE level.

| orbital | energy (eV) | MO contribution (%) | | |
|---|---|---|---|---|
| | | Pt(s/p/d) | C≡CPh-Et-4 | DiBrbpy |
| LUMO+7 | -1.24 | 26.97(9/85/6) | 2.76 | 70.27 |
| LUMO+6 | -1.25 | 17.91(8/81/11) | 3.21 | 78.88 |
| LUMO+5 | -1.48 | 54.02(46/51/3) | 2.15 | 43.83 |
| LUMO+4 | -1.51 | 40.47(38/52/10) | 4.84 | 54.69 |
| LUMO+3 | -1.93 | 21.09(83/5/12) | 4.97 | 73.94 |
| LUMO+2 | -2.20 | 12.58(43/32/25) | 5.23 | 82.19 |
| LUMO+1 | -2.39 | 19.96(58/21/21) | 3.93 | 76.11 |
| LUMO | -2.41 | 13.70(22/46/32) | 3.96 | 82.34 |
| HOMO | -4.98 | 84.63(30/3/67) | 12.08 | 3.29 |
| HOMO-1 | -5.14 | 30.28(5/5/90) | 66.10 | 3.62 |
| HOMO-2 | -5.16 | 28.15(1/7/92) | 68.52 | 3.33 |
| HOMO-3 | -5.31 | 43.84(16/5/79) | 51.33 | 4.83 |
| HOMO-4 | -5.32 | 28.18(4/4/92) | 67.48 | 4.34 |
| HOMO-5 | -5.36 | 36.33(8/5/87) | 55.70 | 7.97 |
| HOMO-6 | -5.41 | 27.94(1/3/96) | 67.05 | 5.01 |
| HOMO-7 | -5.46 | 46.86(24/7/69) | 45.29 | 7.85 |
| HOMO-8 | -5.54 | 34.15(11/9/80) | 58.41 | 7.44 |
| HOMO-9 | -5.88 | 43.56(6/4/90) | 52.02 | 4.42 |
| HOMO-10 | -5.89 | 39.93(0/3/97) | 55.46 | 4.61 |

**Table S15.** Absorption and emission transition properties for the four-molecule model of **1**·1/8($CH_2Cl_2$) in the solid state by TD-DFT method at the PBE1PBE level.

| States | *E*, nm (eV) | O.S. | Component | Contri. | Assignment | Measured Wavelength (nm) |
|---|---|---|---|---|---|---|
| $T_1$ | 719 (1.73) | 0.0000 | HOMO→LUMO | 77% | $^3$MMLCT/$^3$LLCT/$^3$MC | 1022 |
| | | | HOMO→LUMO+2 | 10% | $^3$MMLCT/$^3$LLCT/$^3$MC | |
| | | | HOMO-3→LUMO+1 | 7% | $^3$MMLCT/$^3$LLCT/$^3$MC | |
| $S_1$ | 681 (1.82) | 0.0608 | HOMO→LUMO | 81% | $^1$MLCT/$^1$LLCT/$^1$MC | 761 |
| | | | HOMO→LUMO+2 | 7% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_5$ | 612 (2.03) | 0.0289 | HOMO-2→LUMO | 48% | $^1$MLCT/$^1$LLCT/$^1$MC | 670 |
| | | | HOMO-1→LUMO+1 | 48% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{14}$ | 521 (2.38) | 0.0967 | HOMO-3→LUMO+1 | 45% | $^1$MLCT/$^1$LLCT/$^1$MC | 534 |
| | | | HOMO-7→LUMO | 22% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-4→LUMO+2 | 14% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{15}$ | 518 (2.39) | 0.0413 | HOMO-4→LUMO+2 | 55% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-3→LUMO+1 | 11% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-2→LUMO+3 | 8% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{19}$ | 505 (2.46) | 0.0203 | HOMO-6→LUMO+2 | 34% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-5→LUMO+2 | 15% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-4→LUMO+1 | 11% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-2→LUMO | 11% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-1→LUMO+1 | 11% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{21}$ | 488 (2.5) | 0.0348 | HOMO-5→LUMO+1 | 29% | $^1$MLCT/$^1$LLCT/$^1$MC | 494 |
| | | | HOMO-2→LUMO+2 | 16% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-4→LUMO | 15% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-8→LUMO | 13% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-8→LUMO+2 | 7% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{24}$ | 482 ( 2.57) | 0.0342 | HOMO-6→LUMO+1 | 20% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-8→LUMO | 17% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-9→LUMO+1 | 11% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-10→LUMO | 11% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-8→LUMO+2 | 10% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-4→LUMO+2 | 10% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-4→LUMO | 8% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{32}$ | 460 (2.67) | 0.0291 | HOMO-8→LUMO+2 | 45% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-8→LUMO | 17% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-6→LUMO+1 | 10% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-7→LUMO | 8% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-7→LUMO+2 | 7% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{33}$ | 457 | 0.0854 | HOMO-3→LUMO+3 | 45% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-5→LUMO+3 | 37% | $^1$MLCT/$^1$LLCT/$^1$MC | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | (2.69) | | HOMO-6→LUMO+3 | 7% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{36}$ | 447 (2.77) | 0.0304 | HOMO→LUMO+4 | 83% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{41}$ | 431 (2.88) | 0.0185 | HOMO-5→LUMO+3 | 33% | $^1$MLCT/$^1$LLCT/$^1$MC | 423 |
| | | | HOMO-3→LUMO+3 | 31% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-7→LUMO+2 | 15% | $^1$MLCT/$^1$LLCT/$^1$MC | |

**Table S16.** Partial molecular orbital compositions (%) in the ground state for the five-molecule model of **1**·1/8($CH_2Cl_2$) in the solid state by TD-DFT method at the PBE1PBE level.

| orbital | energy (eV) | MO contribution (%) | | |
|---|---|---|---|---|
| | | Pt(s/p/d) | C≡CPh-Et-4 | DiBrbpy |
| LUMO+6 | -1.48 | 46.45(45/49/6) | 3.34 | 50.21 |
| LUMO+5 | -1.50 | 44.65(27/67/6) | 3.14 | 52.30 |
| LUMO+4 | -1.90 | 21.45(75/12/13) | 4.80 | 73.75 |
| LUMO+3 | -2.00 | 22.51(65/22/13) | 4.93 | 72.56 |
| LUMO+2 | -2.19 | 27.90(60/29/11) | 4.40 | 67.70 |
| LUMO+1 | -2.39 | 19.15(51/27/22) | 3.97 | 76.88 |
| LUMO | -2.46 | 24.84(69/17/14) | 4.44 | 70.72 |
| HOMO | -4.89 | 88.39(31/1/68) | 8.19 | 3.42 |
| HOMO-1 | -5.12 | 30.02(4/5/91) | 66.32 | 3.66 |
| HOMO-2 | -5.14 | 31.84(11/6/83) | 64.22 | 3.94 |
| HOMO-3 | -5.21 | 32.21(6/7/87) | 63.23 | 4.56 |
| HOMO-4 | -5.22 | 58.98(20/6/74) | 38.09 | 2.93 |
| HOMO-5 | -5.33 | 30.59(5/9/86) | 61.55 | 7.86 |
| HOMO-6 | -5.35 | 29.17(6/6/88) | 65.31 | 5.52 |
| HOMO-7 | -5.37 | 26.24(6/4/90) | 68.04 | 5.72 |
| HOMO-8 | -5.42 | 38.85(18/8/74) | 53.00 | 8.15 |
| HOMO-9 | -5.46 | 40.55(11/7/82) | 53.48 | 5.97 |
| HOMO-10 | -5.52 | 36.09(15/7/78) | 56.50 | 7.41 |
| HOMO-11 | -5.77 | 70.82(24/4/72) | 21.78 | 7.40 |

**Table S17.** Absorption and emission transition properties for the five-molecule model of **1**·1/8($CH_2Cl_2$) in the solid state by TD-DFT method at the PBE1PBE level.

| States | *E*, nm (eV) | O.S. | Component | Contri. | Assignment | Measured Wavelength (nm) |
|---|---|---|---|---|---|---|
| $T_1$ | 742 (1.67) | 0.0000 | HOMO→LUMO | 65% | $^3$MMLCT/$^3$LLCT/$^3$MC | 1022 |
| | | | HOMO→LUMO+2 | 11% | | |
| $S_1$ | 708 (1.75) | 0.0715 | HOMO→LUMO | 73% | $^1$MLCT/$^1$LLCT/$^1$MC | 761 |
| | | | HOMO→LUMO+2 | 8% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_2$ | 684 (1.81) | 0.0171 | HOMO→LUMO+1 | 70% | $^1$MLCT/$^1$LLCT/$^1$MC | 670 |
| | | | HOMO-4→LUMO+1 | 7% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{14}$ | 542 (2.29) | 0.049 | HOMO-8→LUMO | 24% | $^1$MLCT/$^1$LLCT/$^1$MC | 534 |
| | | | HOMO-4→LUMO | 17% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-2→LUMO+2 | 9% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-3→LUMO+2 | 8% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_6$ | 529 (2.34) | 0.074 | HOMO-5→LUMO+1 | 24% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-4→LUMO+1 | 21% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-8→LUMO+1 | 14% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-6→LUMO+1 | 14% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{26}$ | 493 (2.52) | 0.0431 | HOMO-5→LUMO+2 | 17% | $^1$MLCT/$^1$LLCT/$^1$MC | 494 |
| | | | HOMO-3→LUMO+3 | 12% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-9→LUMO+1 | 7% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-6→LUMO+2 | 6% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-10→LUMO+1 | 5% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{40}$ | 466 (2.66) | 0.0343 | HOMO-4→LUMO+4 | 37% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-7→LUMO+3 | 13% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-10→LUMO+2 | 6% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{45}$ | 452 (2.74) | 0.0376 | HOMO→LUMO+5 | 49% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO→LUMO+6 | 24% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{46}$ | 450 (2.76) | 0.0258 | HOMO-11→LUMO | 23% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO→LUMO+6 | 10% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-10→LUMO+1 | 8% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-8→LUMO+3 | 8% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-11→LUMO+2 | 7% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{48}$ | 449 (2.76) | 0.0291 | HOMO-11→LUMO | 12% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-6→LUMO+4 | 11% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO→LUMO+6 | 11% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-8→LUMO+2 | 8% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| $S_{51}$ | 444 (2.79) | 0.037 | HOMO-10→LUMO+1 | 28% | $^1$MLCT/$^1$LLCT/$^1$MC | 423 |
| | | | HOMO-10→LUMO+3 | 14% | $^1$MLCT/$^1$LLCT/$^1$MC | |
| | | | HOMO-9→LUMO+1 | 13% | $^1$MLCT/$^1$LLCT/$^1$MC | |

| | | | |
|---|---|---|---|
| | HOMO-9→LUMO+3 | 8% | $^1$MLCT/$^1$LLCT/$^1$MC |
| | HOMO-10→LUMO+2 | 7% | $^1$MLCT/$^1$LLCT/$^1$MC |

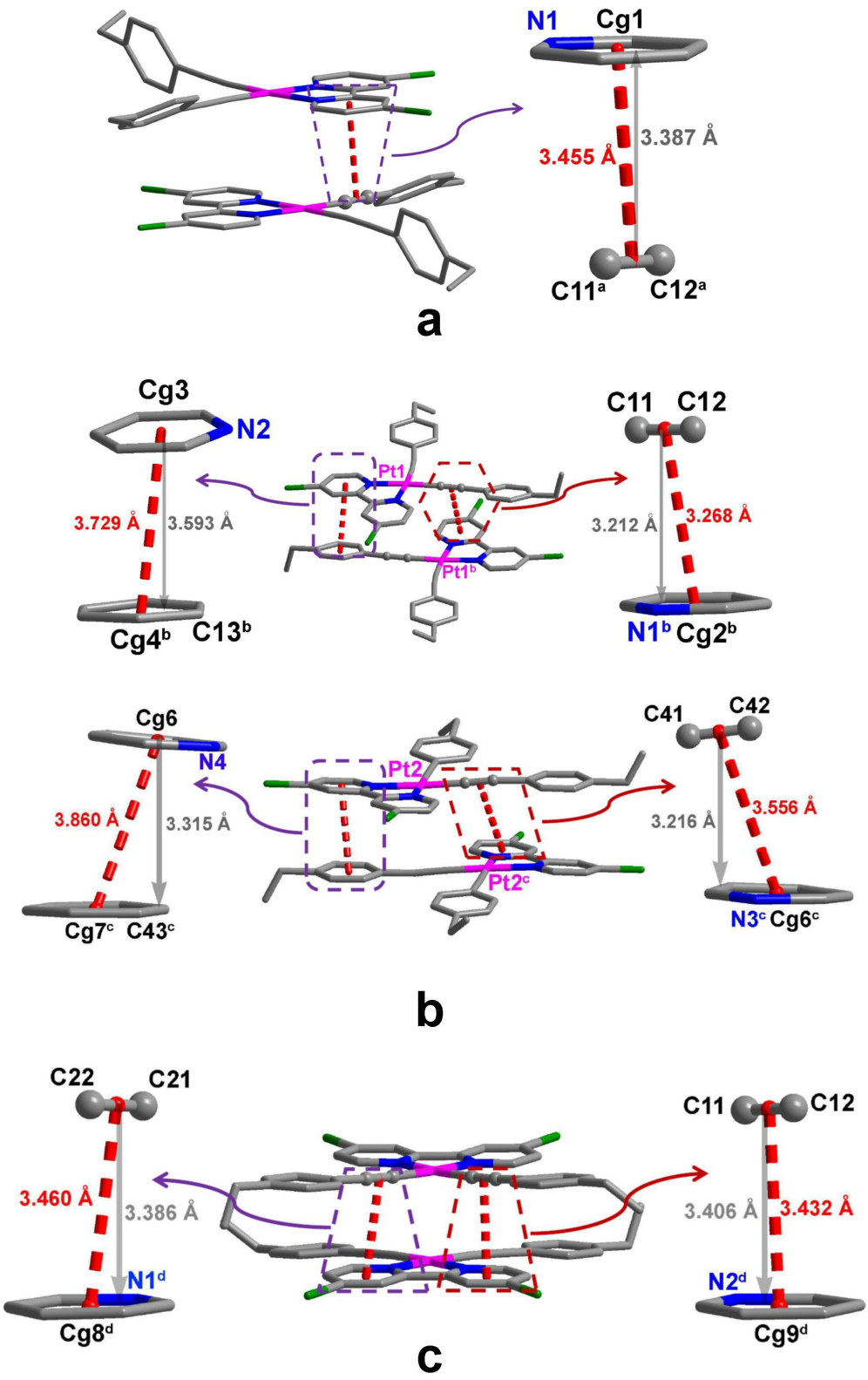



**Figure S1.** The $\pi$-$\pi$ stacking interactions within the quasi-dimeric structure of **1**·DMSO (a) and dimeric structure of **1**·1/2($CH_3CN$) (b), and one dimeric unit showing the $\pi$-$\pi$ stacking interactions in the 1-D linear chain of **1**·1/8($CH_2Cl_2$) (c). The hydrogen atoms are omitted for clarity. Symmetry code: a. 2-x, 1-y, 2-z; b. 1-x, -y, -z; c. 1-x, 1-y,1- z; d. -x, 1-y, 1-z.

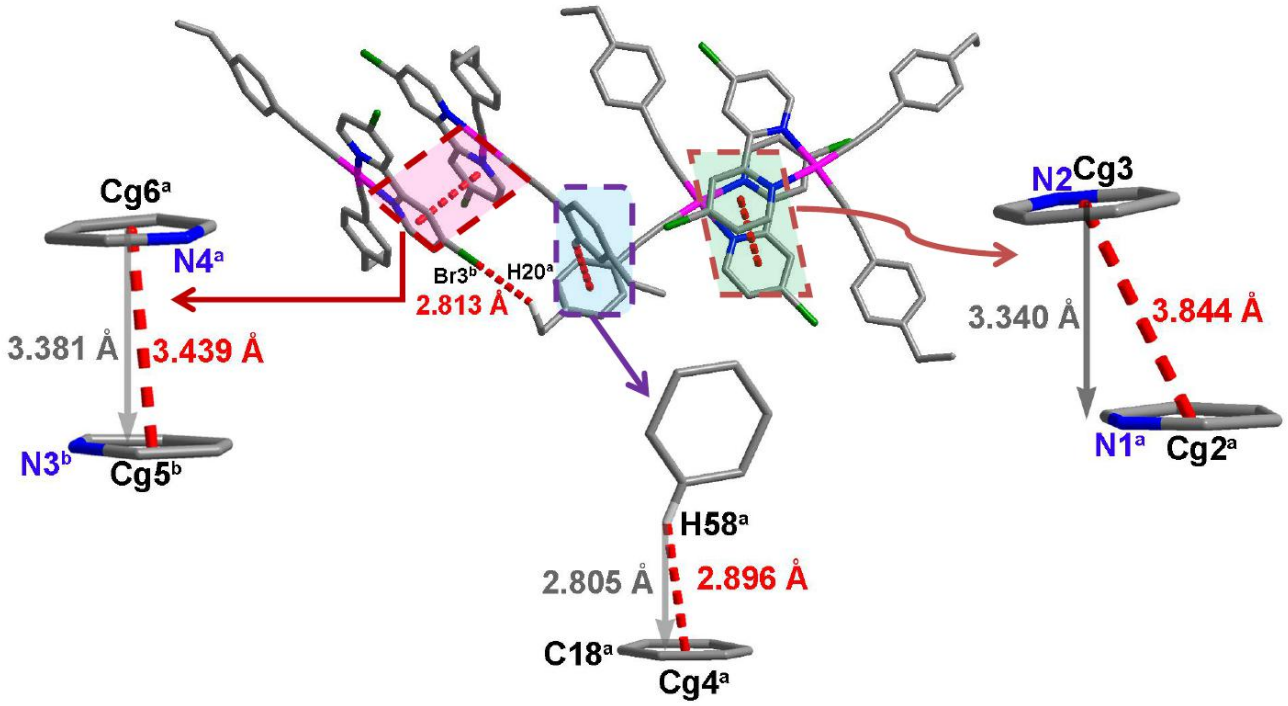



**Figure S2.** The interactions between adjacent dimeric structures in complex **1**·1/2($CH_3CN$). The hydrogen atoms not participate in hydrogen bond are omitted for clarity. Symmetry code: a. -x, -y, -z; b. -2+x, -1+y, -1+z.

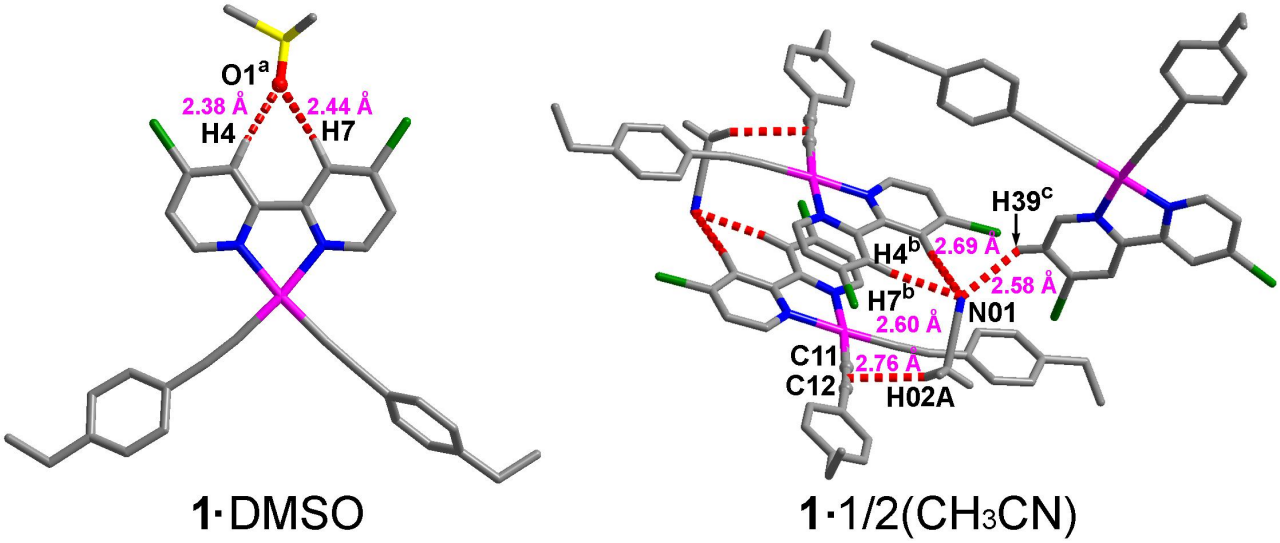



**Figure S3.** The hydrogen bonds between solvate molecules and Pt(II) moieties in complex **1**·DMSO and **1**·1/2($CH_3CN$). The hydrogen atoms not important are omitted for clarity. Symmetry code: a. x, y, 1+z; b. -x, -y, -z; c. -1+x, y, z.

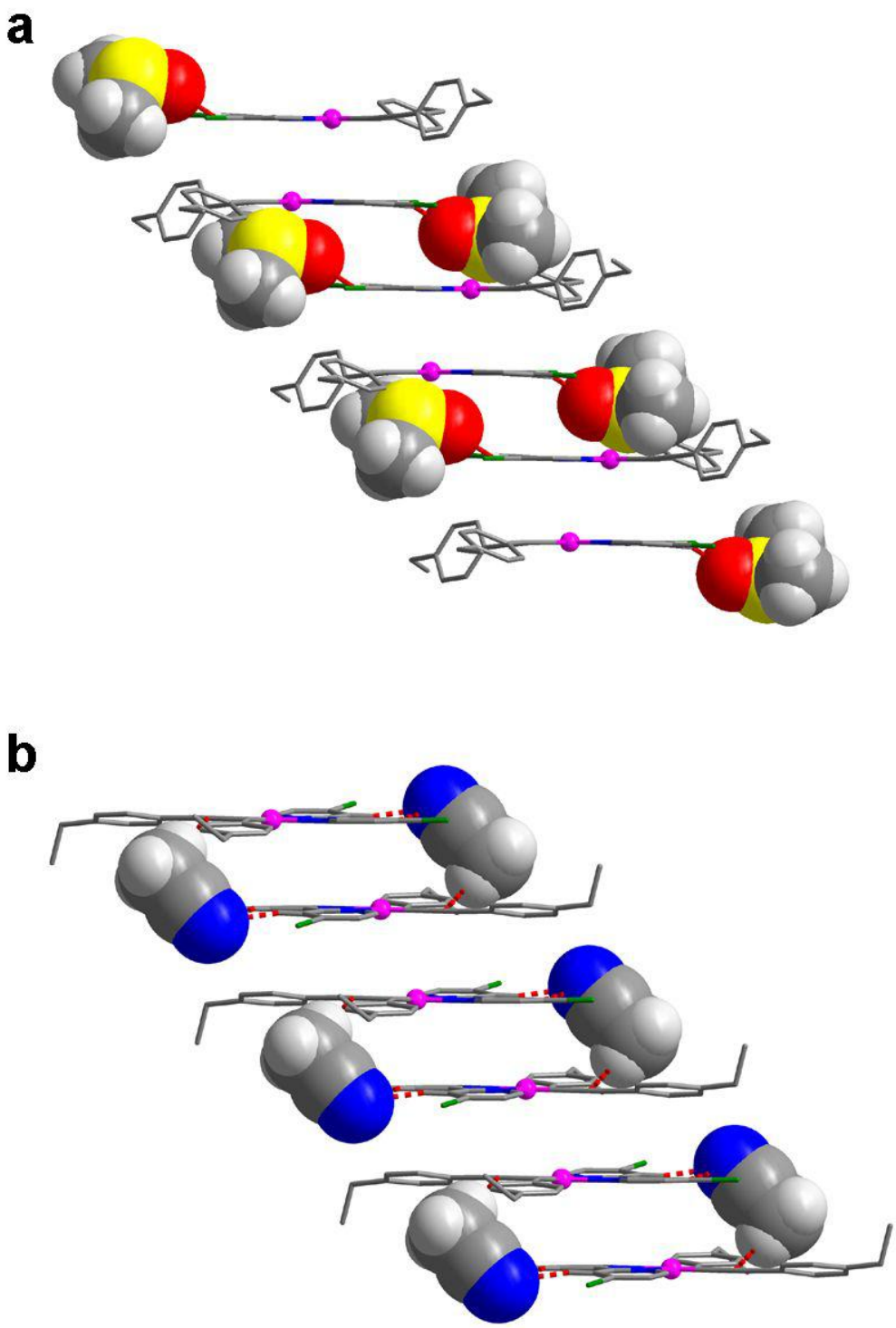



**Figure S4.** Packing diagrams of **1**·DMSO (a) and **1**·1/2($CH_3CN$) (b), showing the Pt(II) moieties are well separated by the solvent molecules in the two phases.

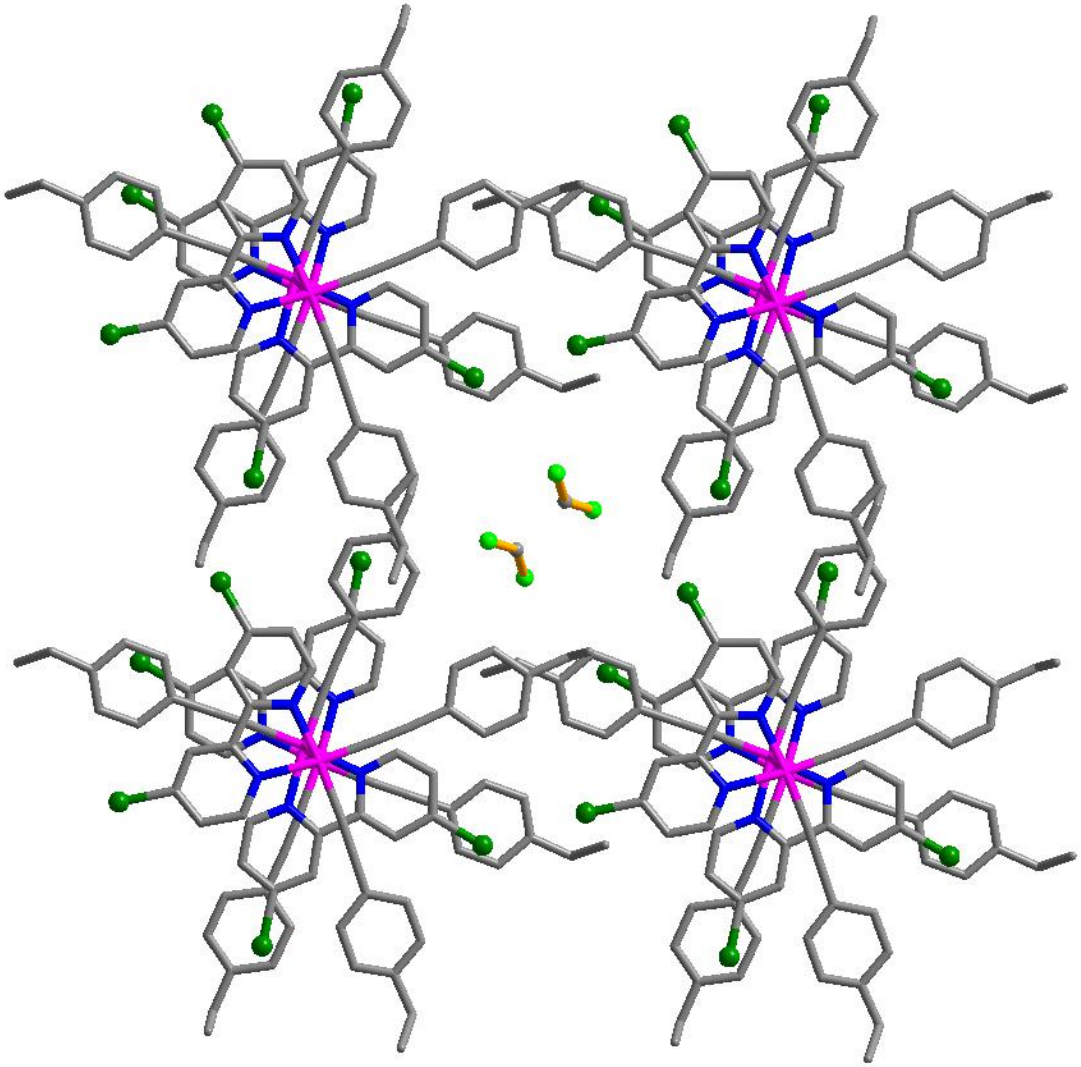


**Figure S5.** The stacking diagram of **1**·1/8($CH_2Cl_2$), showing the $CH_2Cl_2$ solvate molecules located in space of crystal lattice.

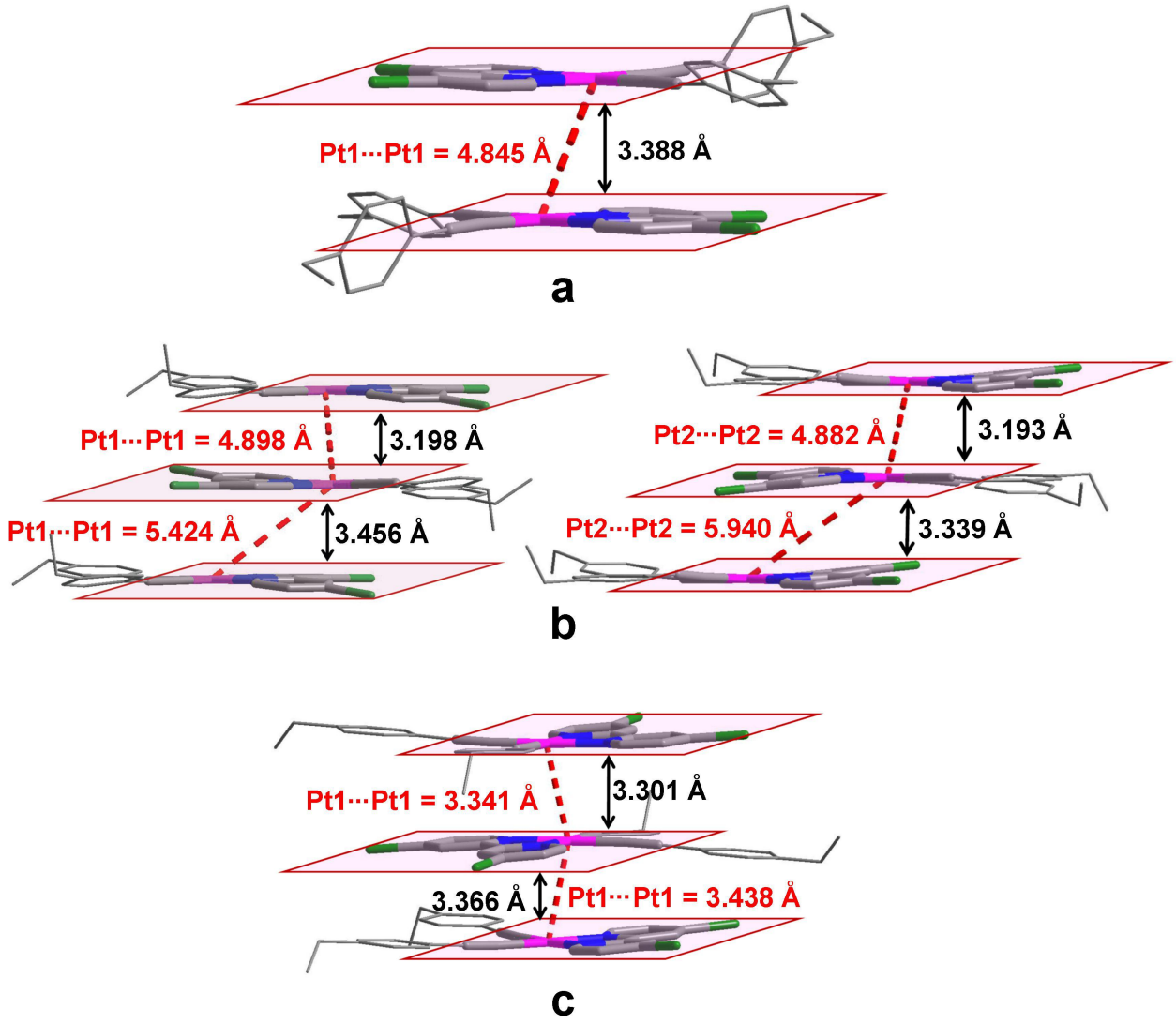



**Figure S6.** The Pt···Pt distances and interplanar distances in the stacking structures of **1**·DMSO (a), **1**·1/2($CH_3CN$) (b), and **1**·1/8($CH_2Cl_2$) (c).

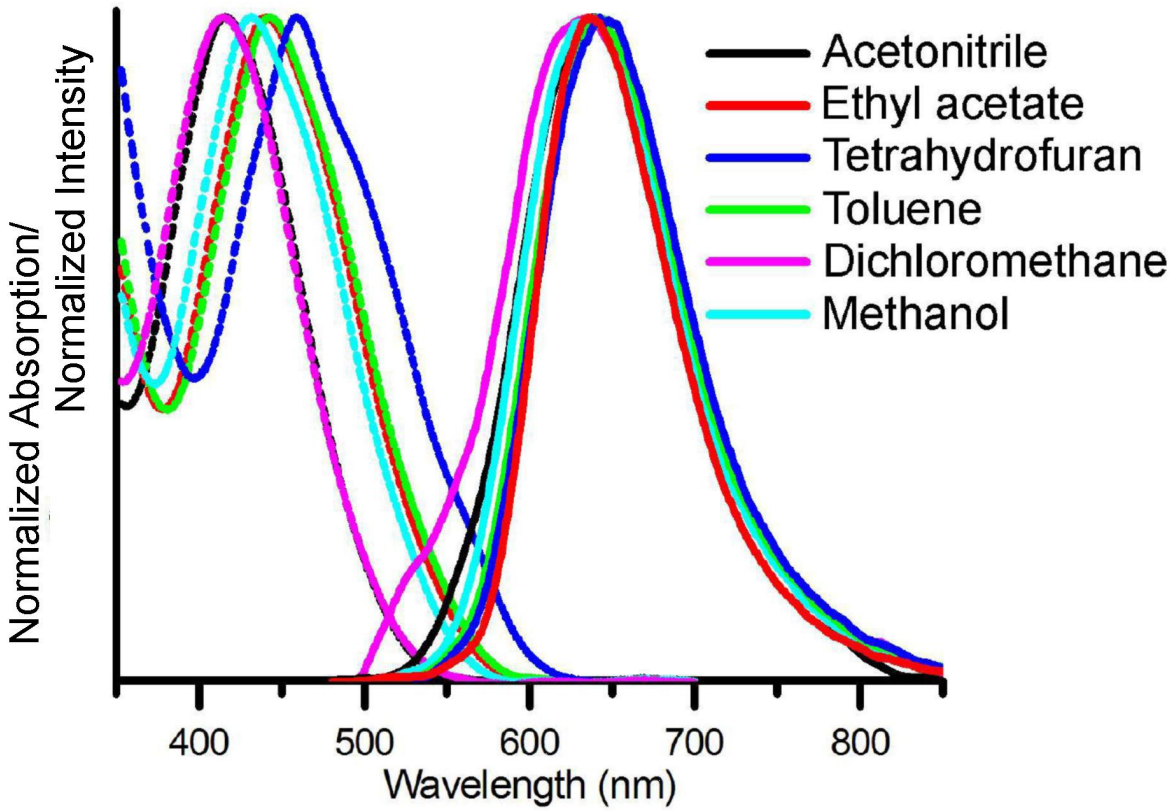



**Figure S7.** Low-energy absorption (dash lines) and emission spectra (solid lines) of **1** in various solvents at ambient temperature.

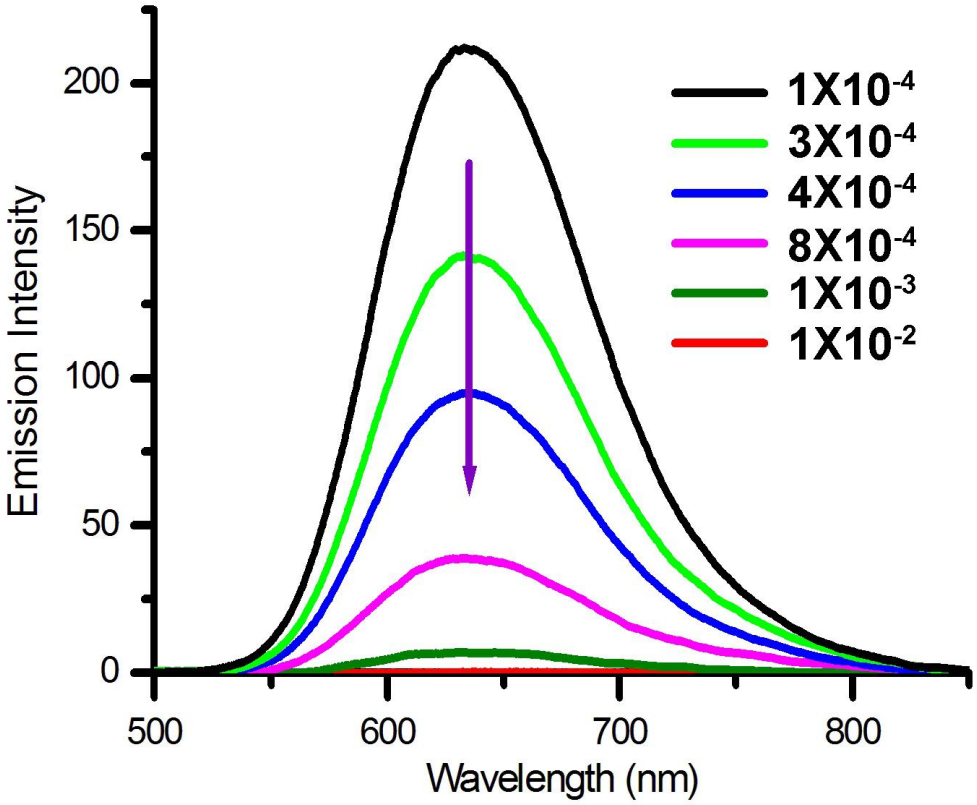



**Figure S8.** Emission spectra of **1** in dichloromethane solution with different concentration.

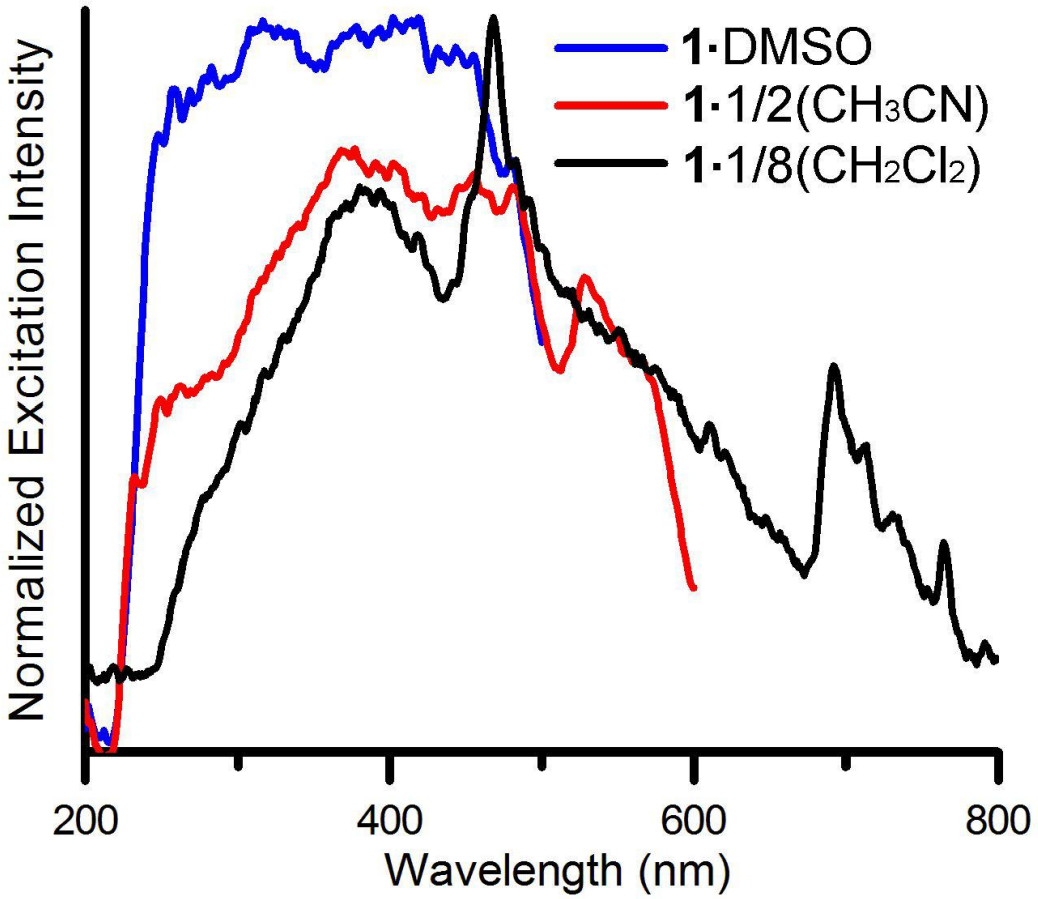



**Figure S9.** The excitation spectra of solid samples **1**·DMSO, **1**·1/2($CH_3CN$), and **1**·1/8($CH_2Cl_2$) at ambient temperature.

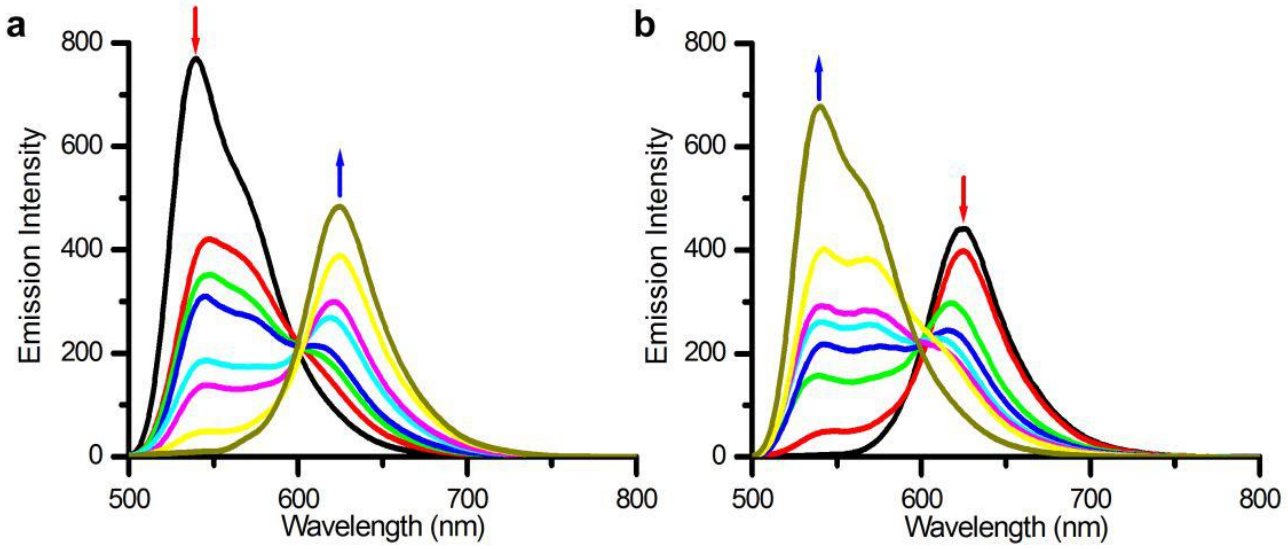



**Figure S10.** Emission spectral changes of solid **1**·DMSO in response to $CH_3CN$ vapor (left) and **1**·1/2($CH_3CN$) to DMSO vapor (right), showing gradual interconversions between two vibronic-structured emission bands (540 and 570 nm) and a broad unstructured emission band (625 nm).

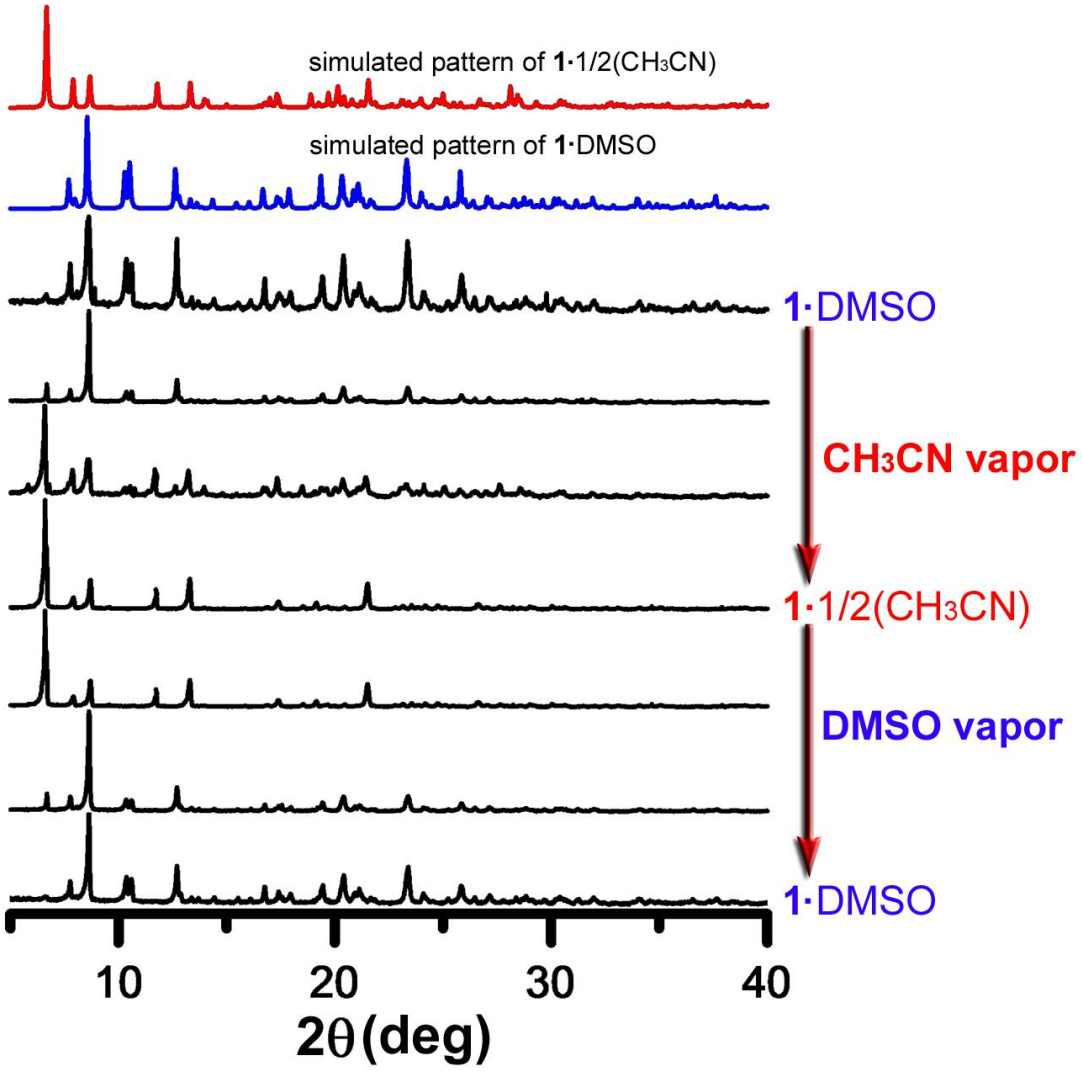



**Figure S11.** The XRD diagrams recorded in a reversible vapochromic cycle **1**·DMSO⇆**1**·1/2($CH_3CN$), showing dynamic variations of XRD patterns from **1**·DMSO→**1**·1/2($CH_3CN$) upon exposure of **1**·DMSO into a saturated $CH_3CN$ vapor, and the XRD patterns from **1**·1/2($CH_3CN$)→**1**·DMSO by exposing **1**·1/2($CH_3CN$) into DMSO vapor at ambient temperature.

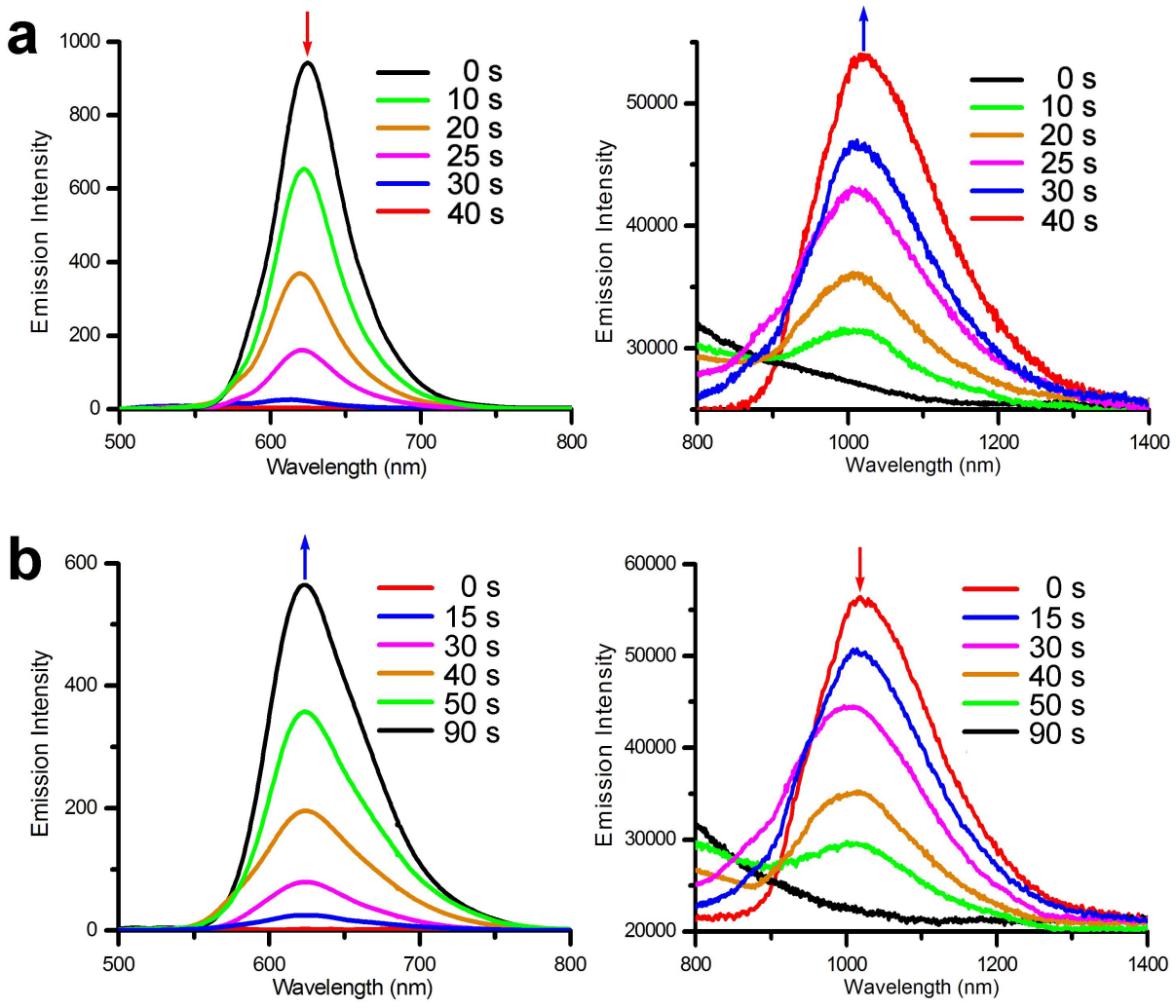



**Figure S12.** Emission spectral changes (left is in visible region and right is in NIR region) of solid **1**·1/2($CH_3CN$) sample in response to $CH_2Cl_2$ vapor (a) and **1**·1/8($CH_2Cl_2$) in response to $CH_3CN$ vapor (b), showing gradual interconversions between emission bands in visible region (625 nm) and in NIR region (1022 nm).

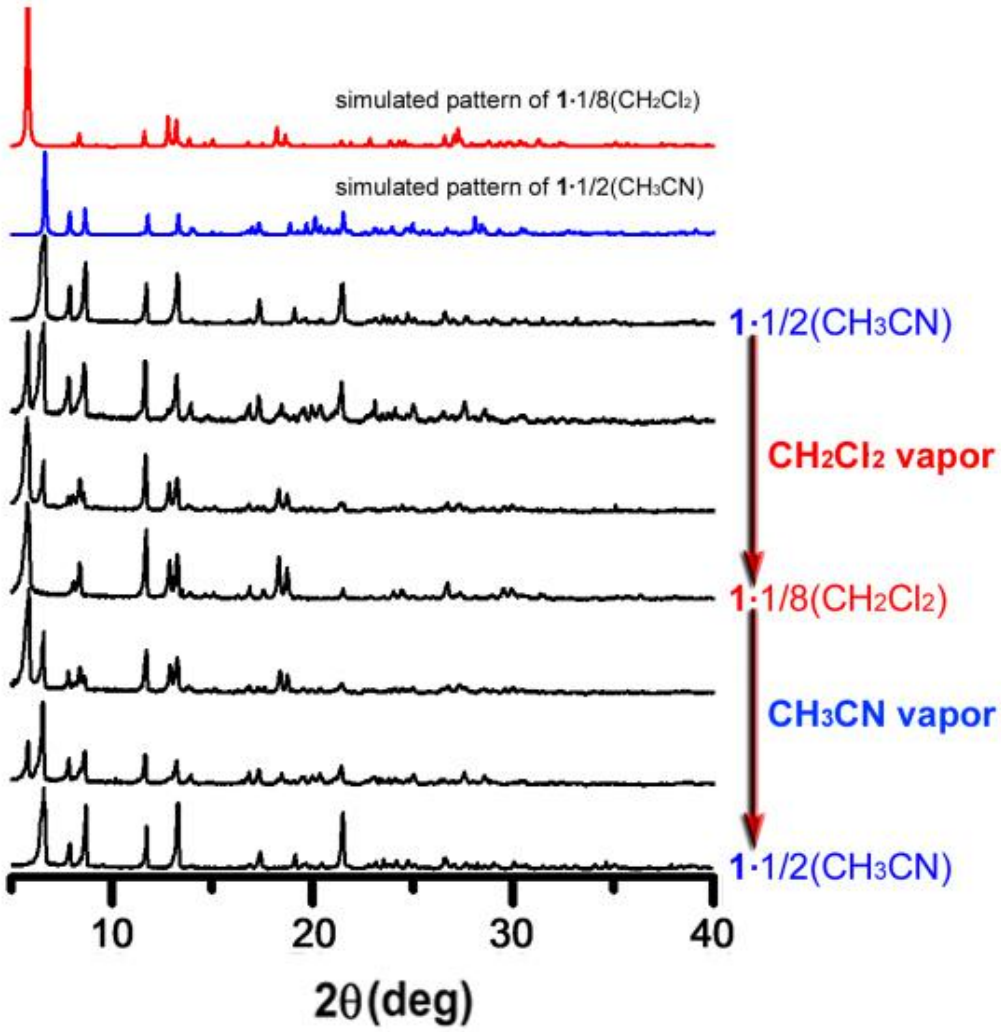



**Figure S13.** The XRD diagrams recorded in a reversible vapochromic cycle **1**·1/2($CH_3CN$) ⇆ **1**·1/8($CH_2Cl_2$), showing dynamic variations of XRD patterns from **1**·1/2($CH_3CN$)→**1**·1/8($CH_2Cl_2$) upon exposure of **1**·1/2($CH_3CN$) into a saturated $CH_2Cl_2$ vapor, and the XRD patterns from **1**·1/8($CH_2Cl_2$)→**1**·1/2($CH_3CN$) by exposing **1**·1/8($CH_2Cl_2$) into $CH_3CN$ vapor at ambient temperature.

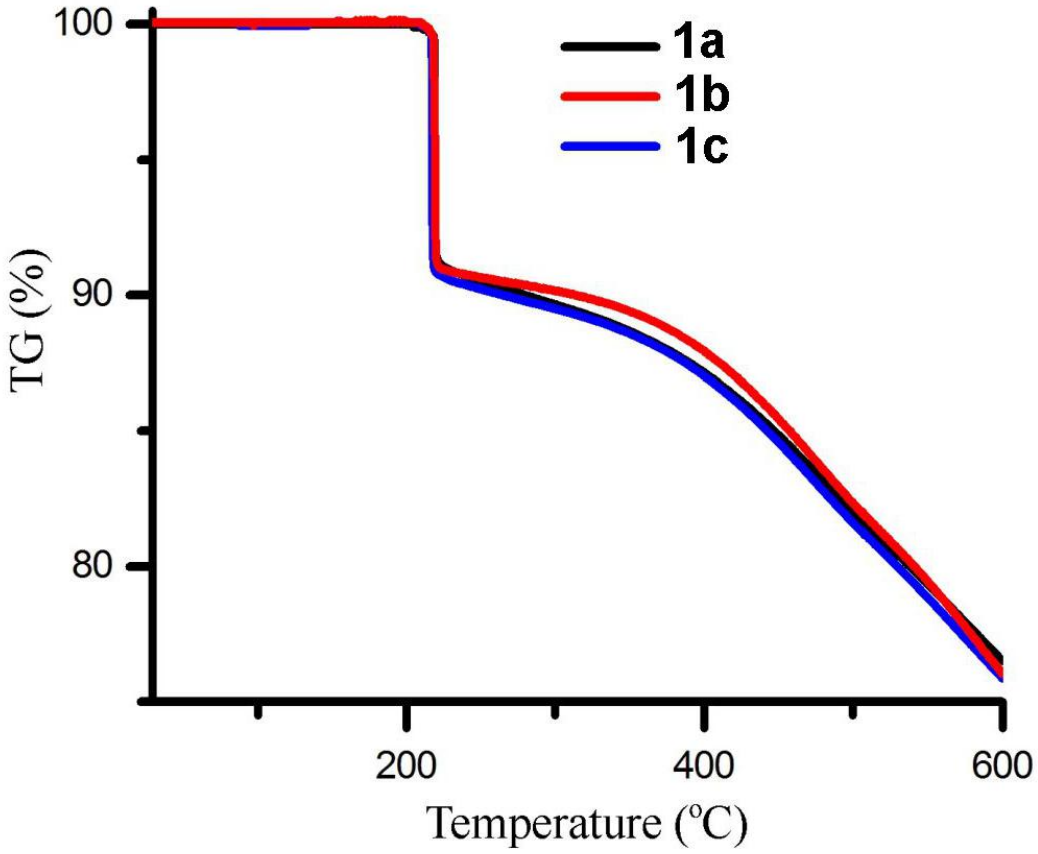
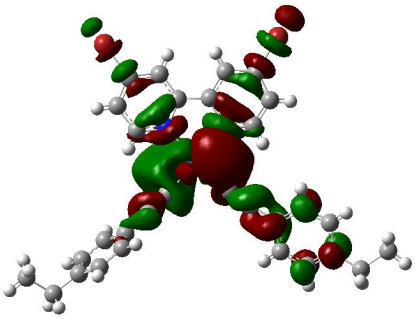
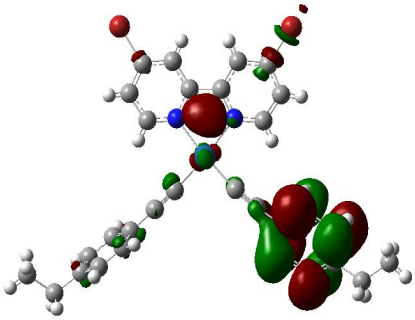


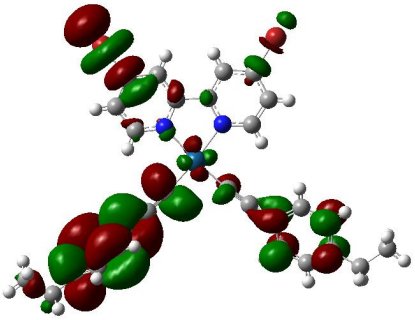

**Figure S14.** Thermogravimetric analysis curves of the three heated samples **1a**, **1b** and **1c**.



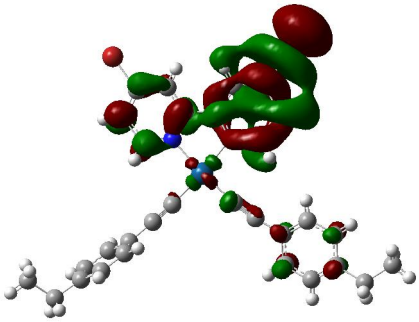
LUMO+11



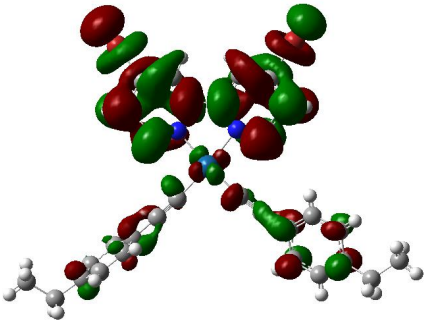
LUMO+8



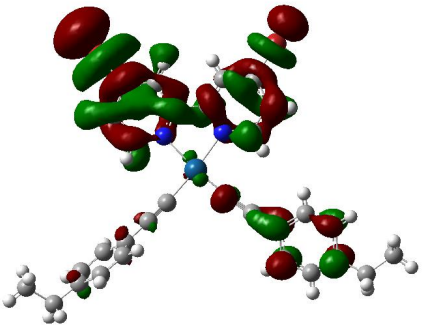
LUMO+7



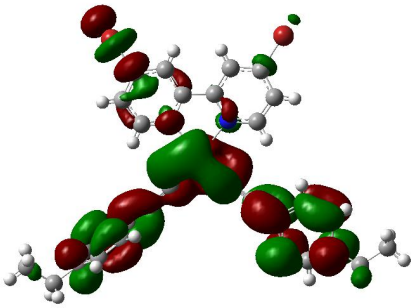
LUMO+6



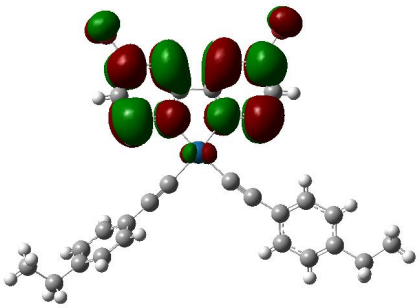
LUMO+5



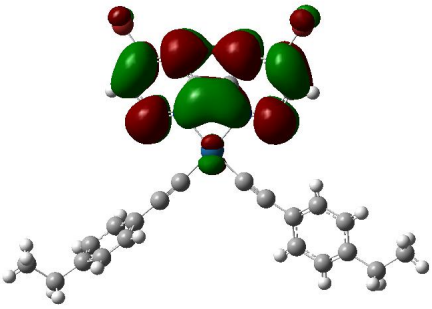
LUMO+4



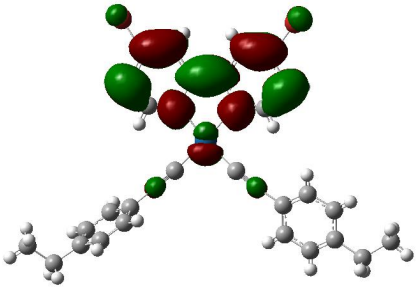
LUMO+3



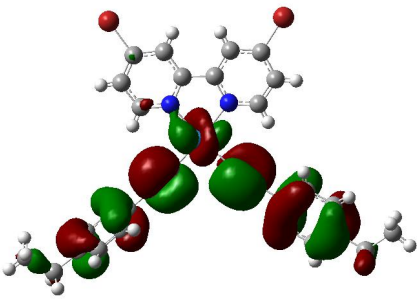
LUMO+2



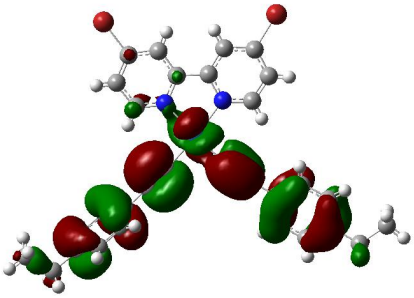
LUMO+1



LUMO



HOMO



HOMO-1

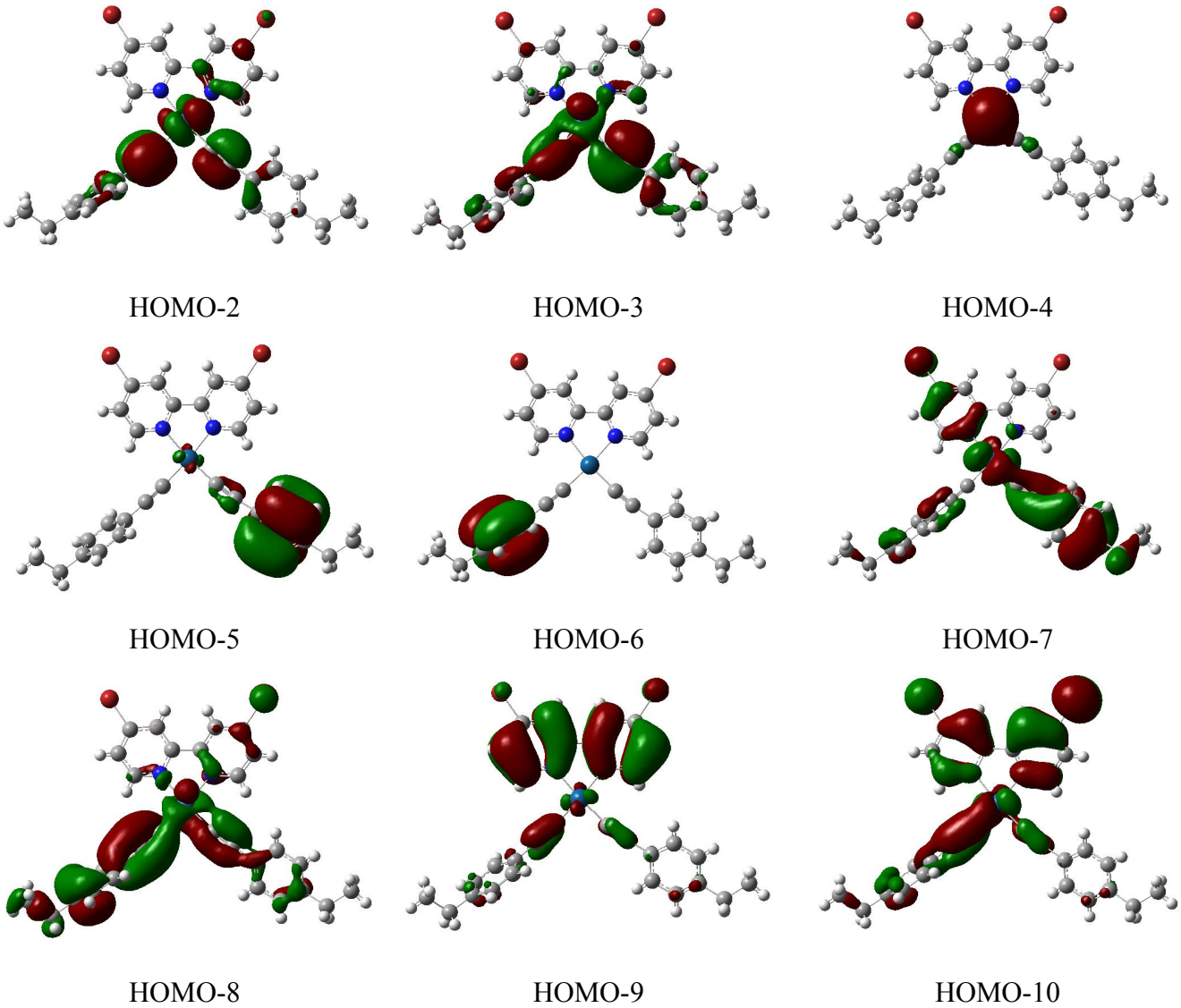
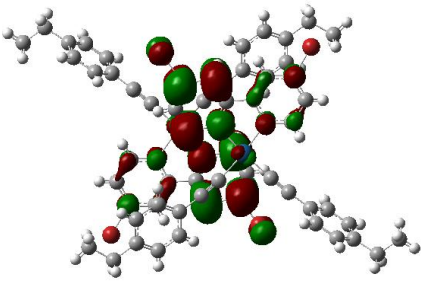
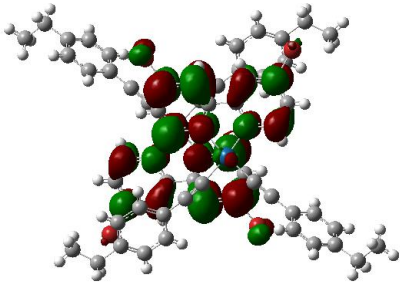


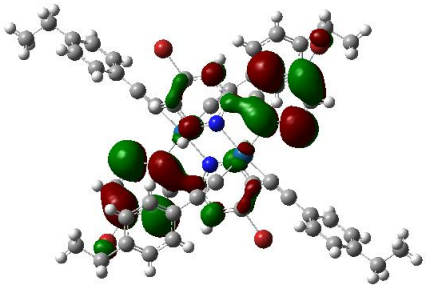

**Figure S15.** Plots of the frontier molecular orbitals involved in the absorption transition for complex **1** in dichloromethane solution (isovalue = 0.02).



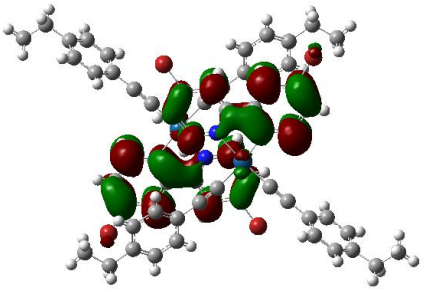
LUMO+5



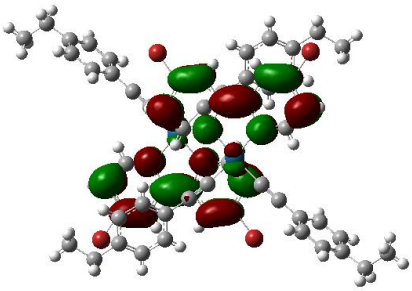
LUMO+4



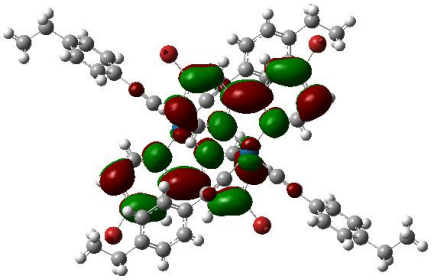
LUMO+3



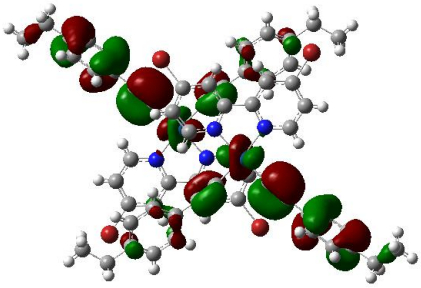
LUMO+2



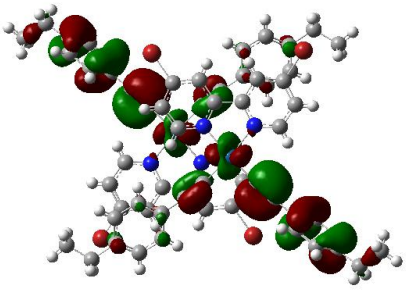
LUMO+1



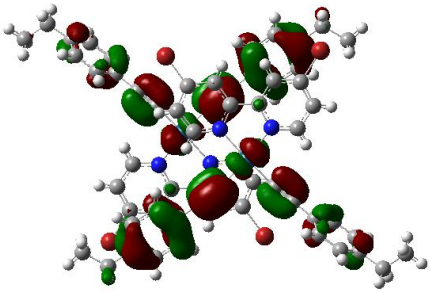
LUMO



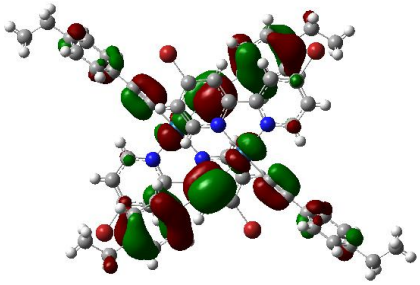
HOMO



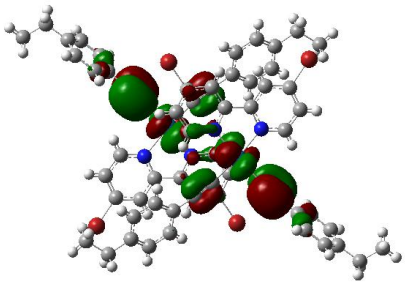
HOMO-1



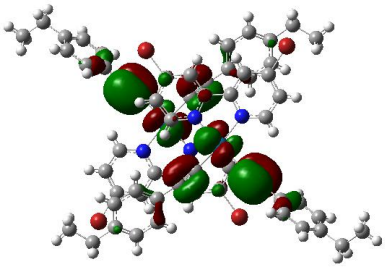
HOMO-2



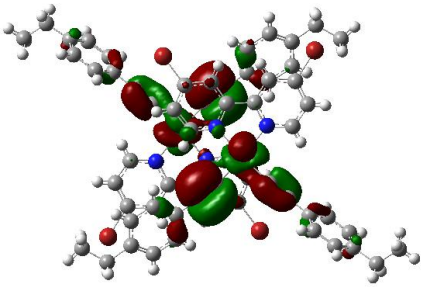
HOMO-3



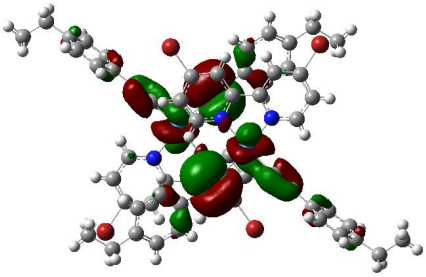
HOMO-4



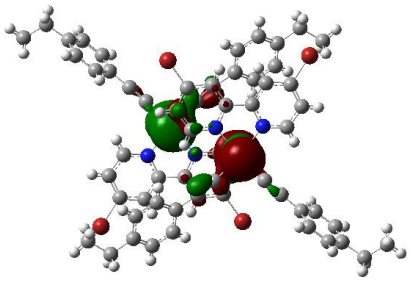
HOMO-5



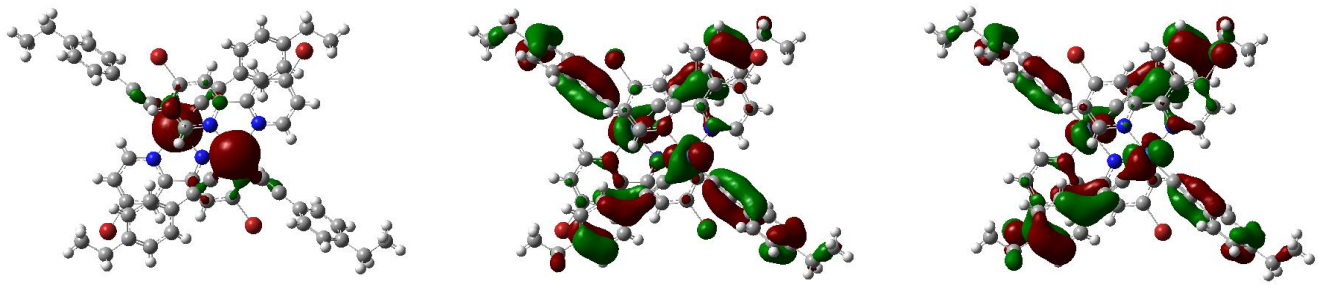
HOMO-6



HOMO-7

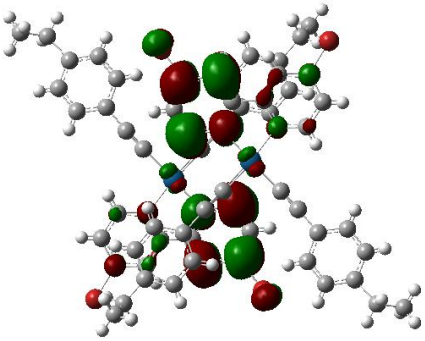


HOMO-8

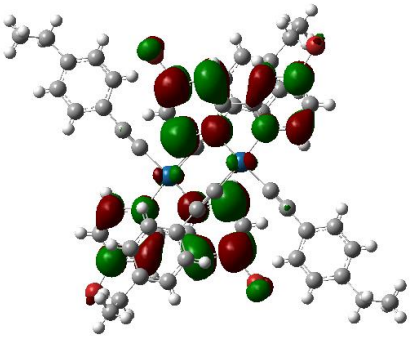


HOMO-9 HOMO-14 HOMO-15

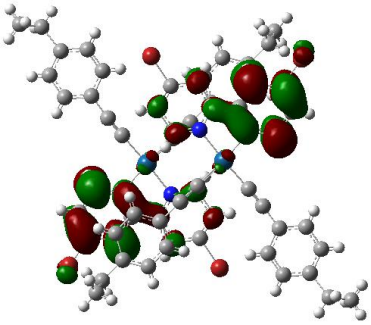
**Figure S16.** Plots of the frontier molecular orbitals involved in the absorption transition for the two-molecule model of **1**·DMSO (isovalue = 0.02).



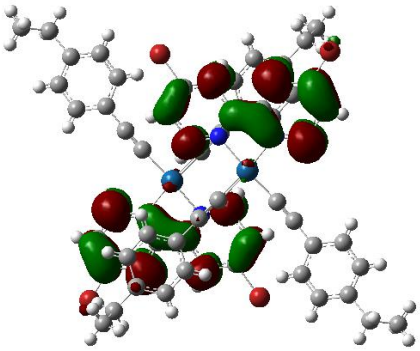
LUMO+5



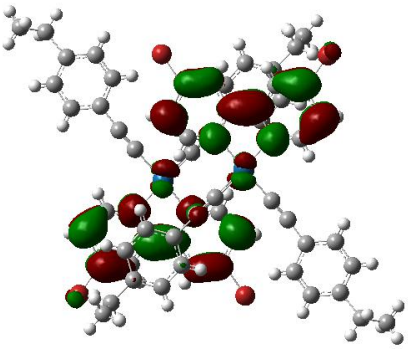
LUMO+4



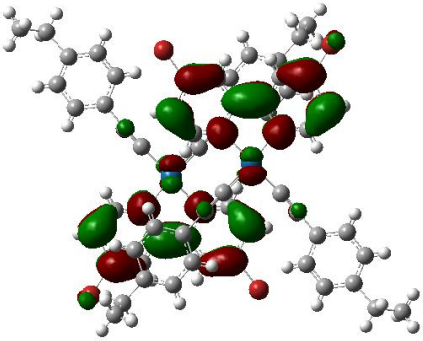
LUMO+3



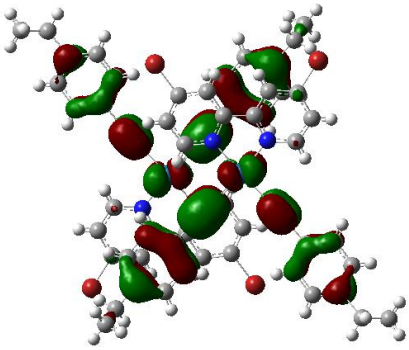
LUMO+2



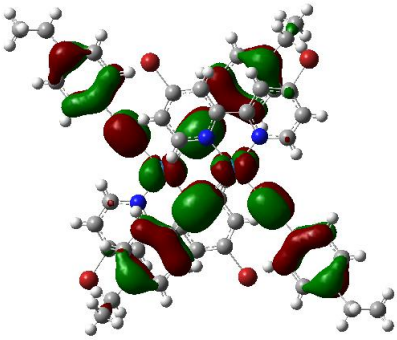
LUMO+1



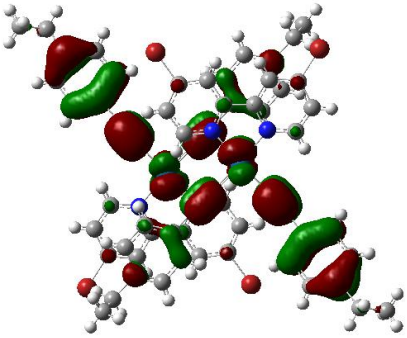
LUMO



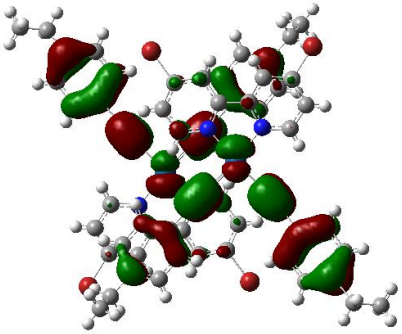
HOMO



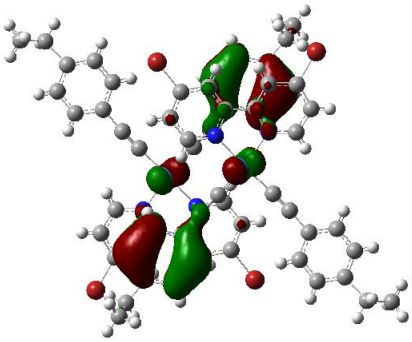
HOMO-1



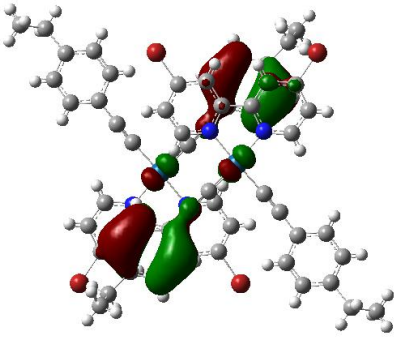
HOMO-2



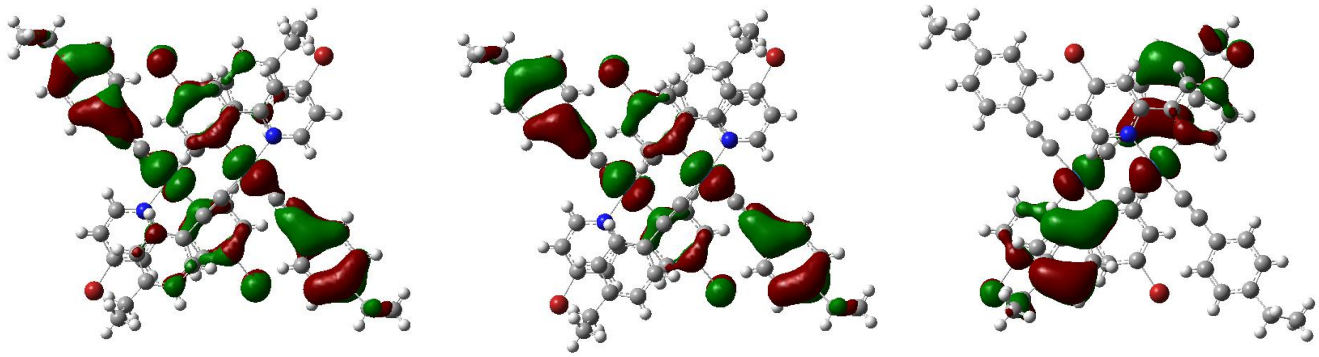
HOMO-3



HOMO-12

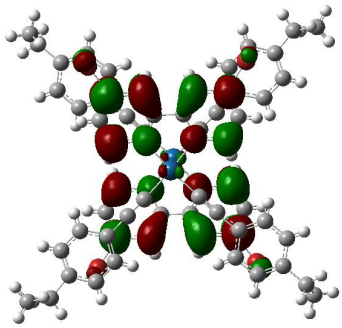


HOMO-13

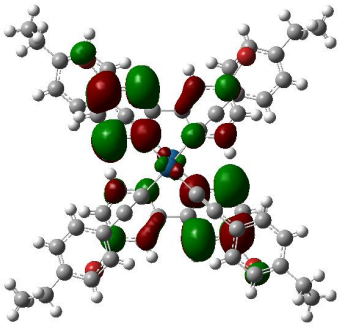


HOMO-14 HOMO-15 HOMO-16

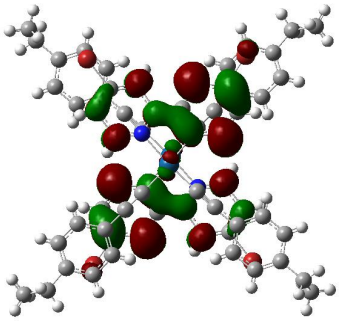
**Figure S17.** Plots of the frontier molecular orbitals involved in the absorption transition for the two-molecule model of **1**·1/2($CH_3CN$) (isovalue = 0.02).



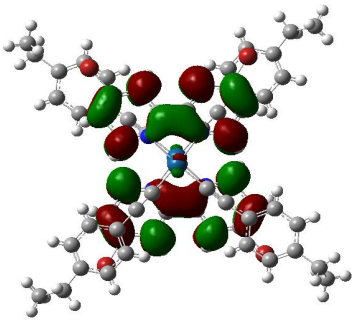
LUMO+5



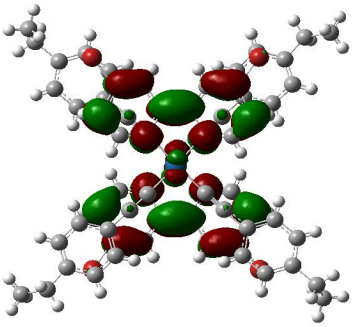
LUMO+4



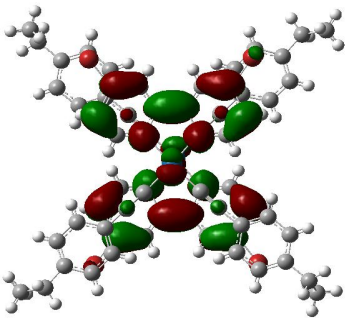
LUMO+3



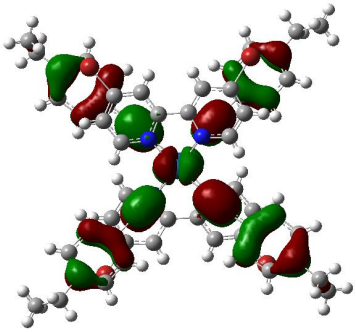
LUMO+2



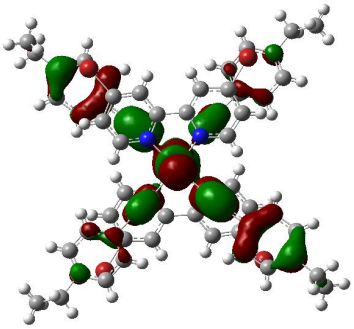
LUMO+1



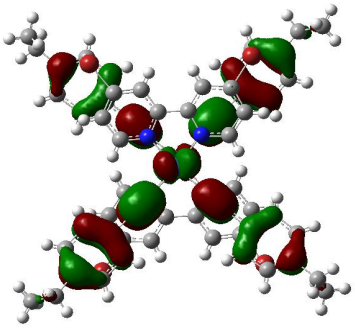
LUMO



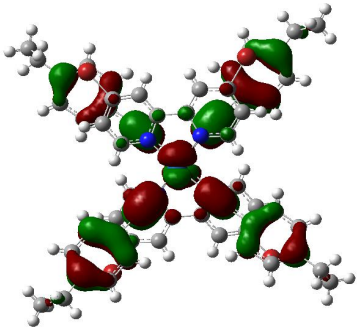
HOMO



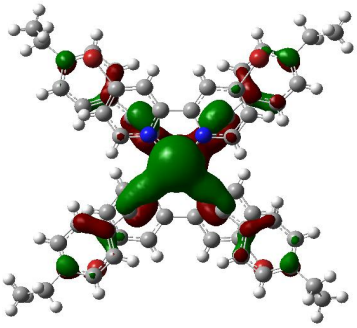
HOMO-1



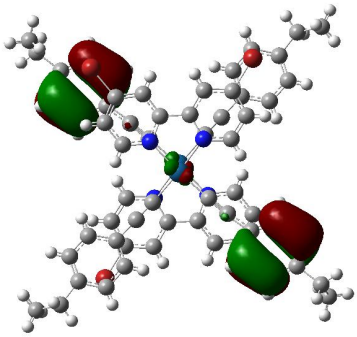
HOMO-2



HOMO-3



HOMO-4



HOMO-9

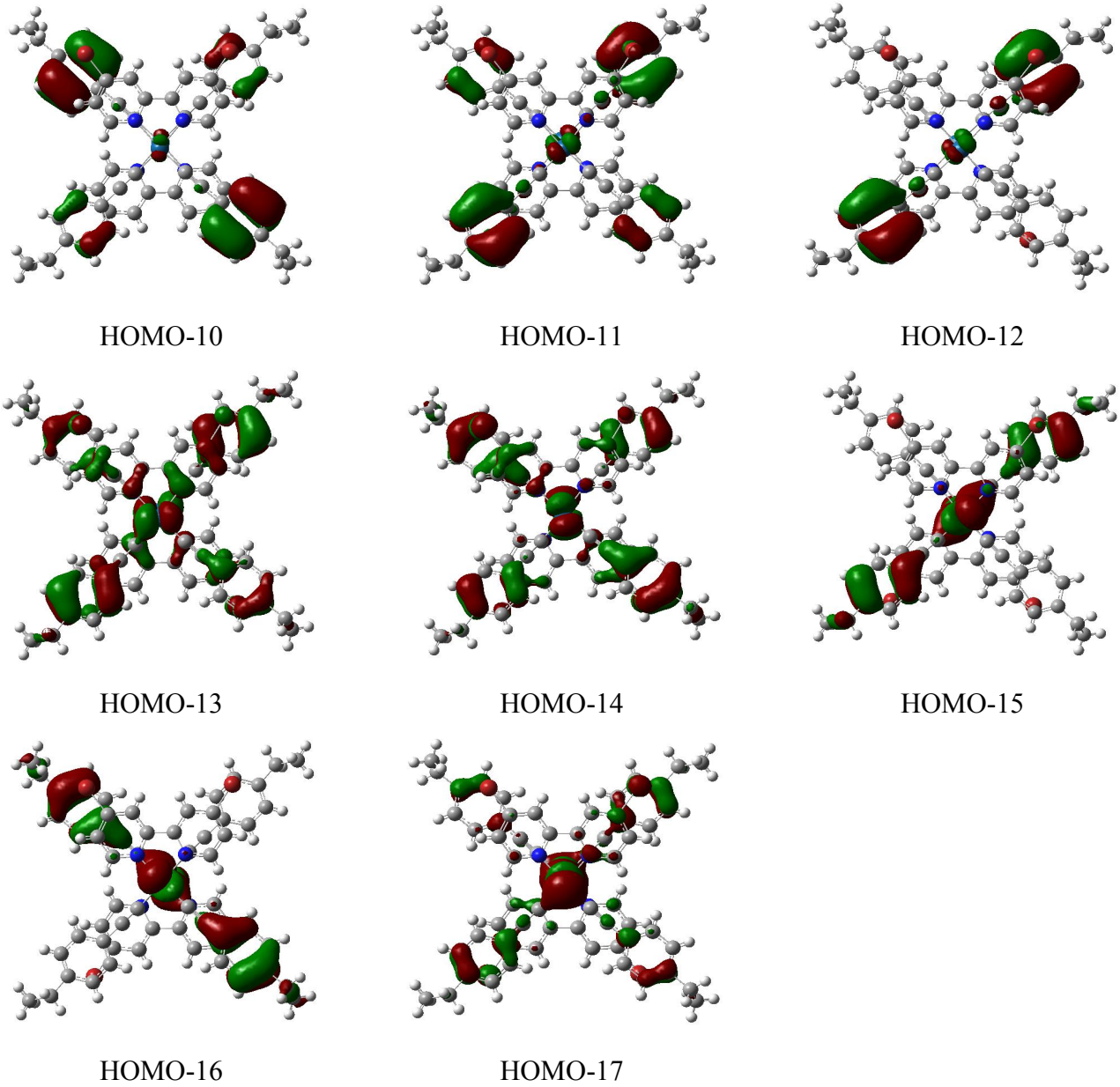
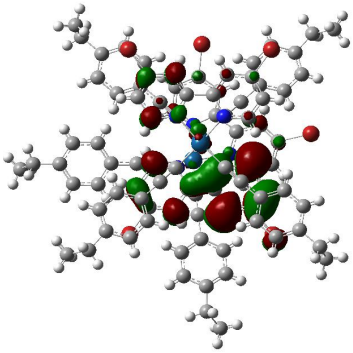
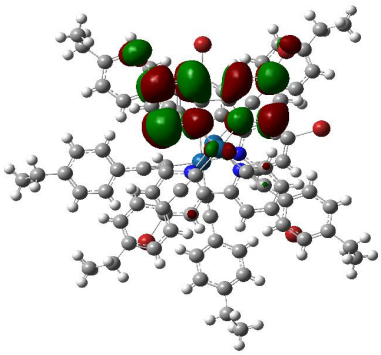


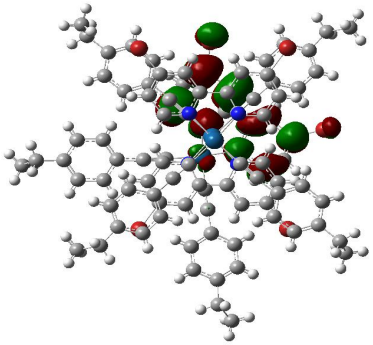

**Figure S18.** Plots of the frontier molecular orbitals involved in the absorption transition for two-molecule model of **1**·1/8($CH_2Cl_2$) (isovalue = 0.02).



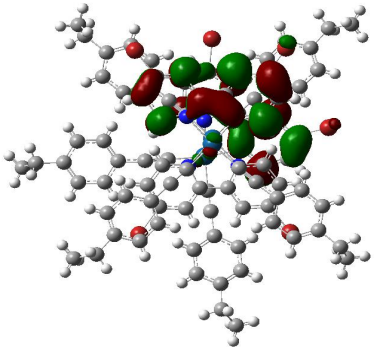
LUMO+7



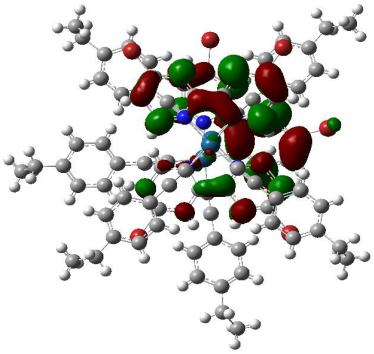
LUMO+6



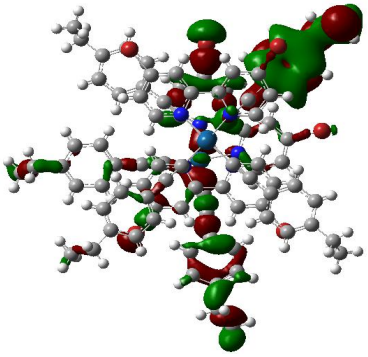
LUMO+5



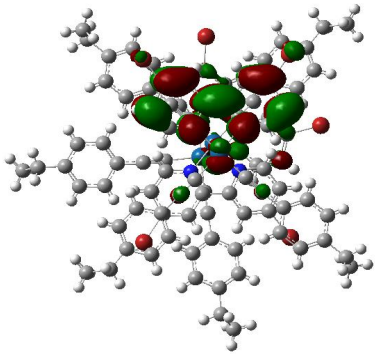
LUMO+4



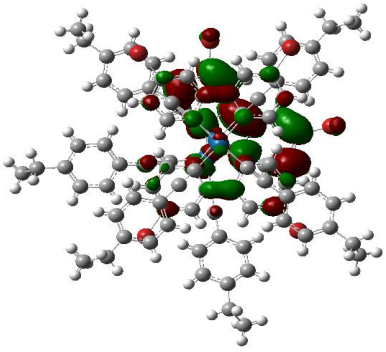
LUMO+3



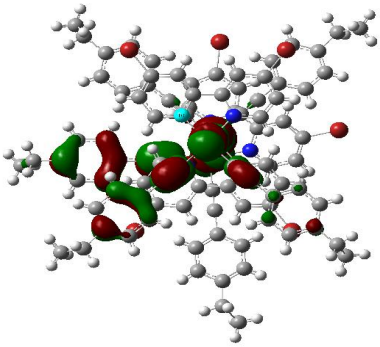
LUMO+2



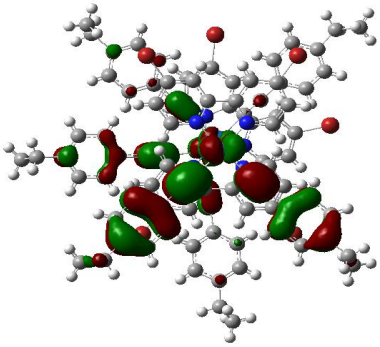
LUMO+1



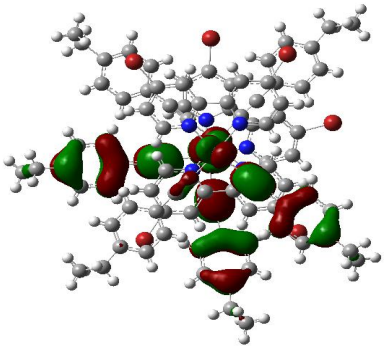
LUMO



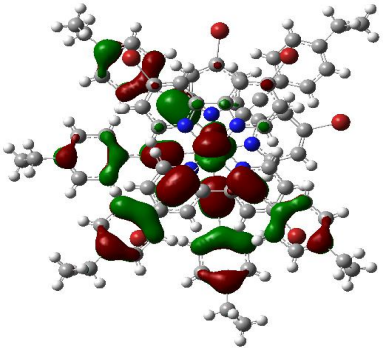
HOMO



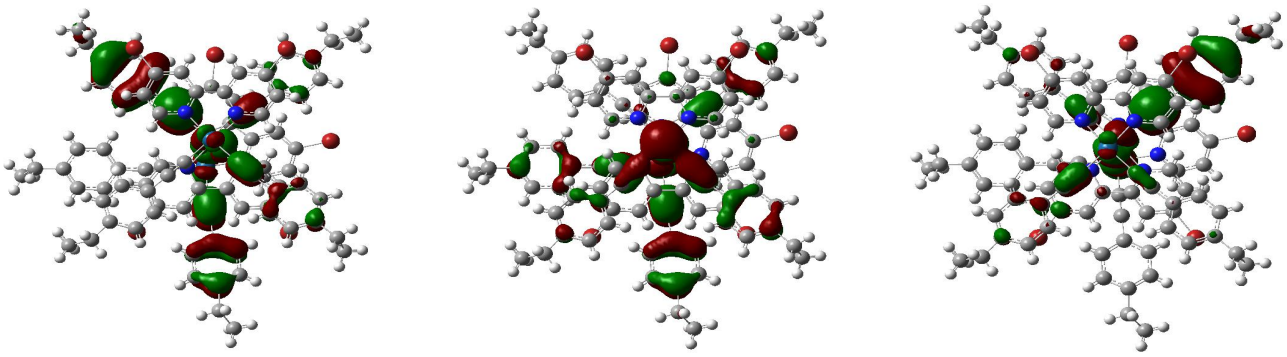
HOMO-1



HOMO-2

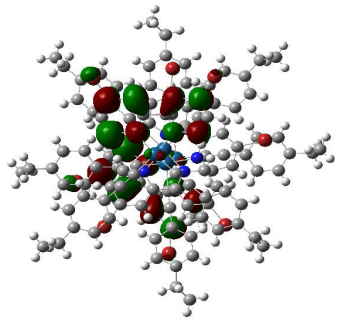


HOMO-3

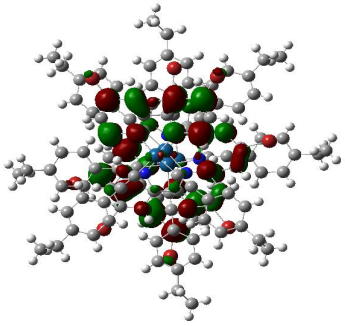


HOMO-4 HOMO-5 HOMO-6

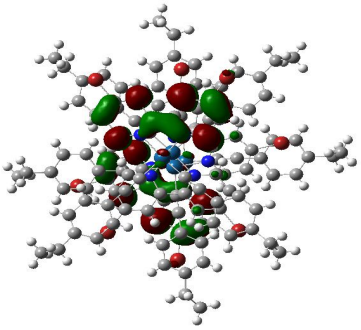
**Figure S19.** Plots of the frontier molecular orbitals involved in the absorption transition for three-molecule model of **1**·1/8($CH_2Cl_2$) (isovalue = 0.02).



LUMO+7



LUMO+6



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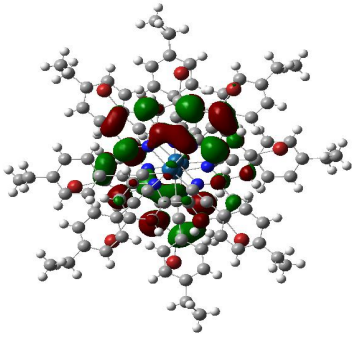

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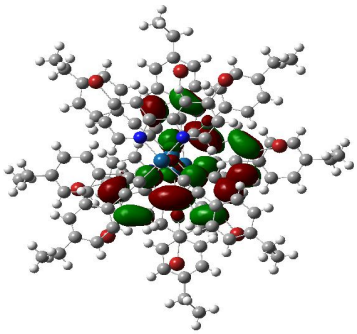

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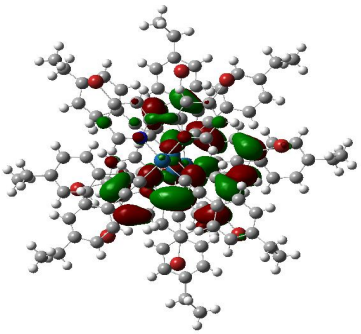

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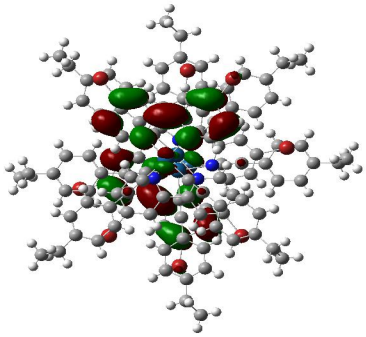

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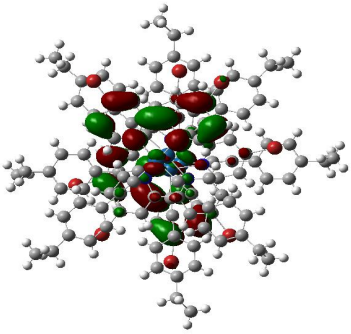

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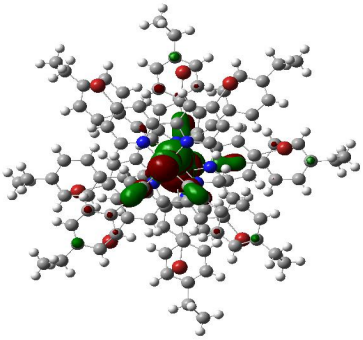

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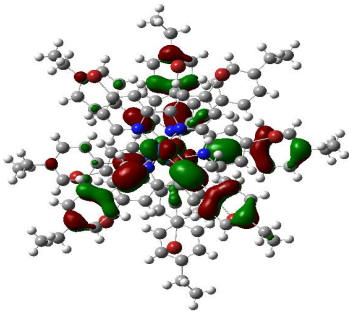

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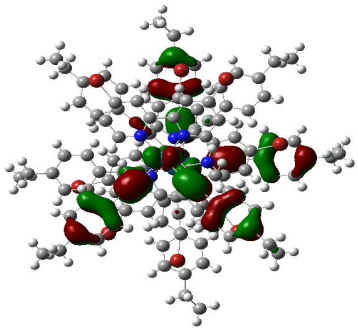

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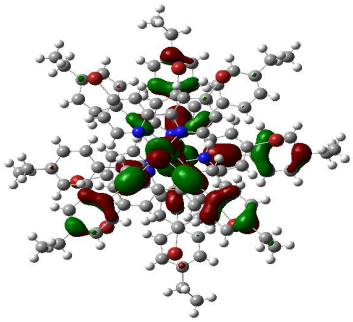

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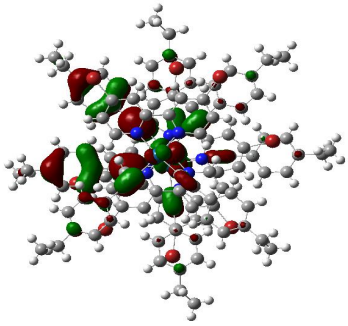

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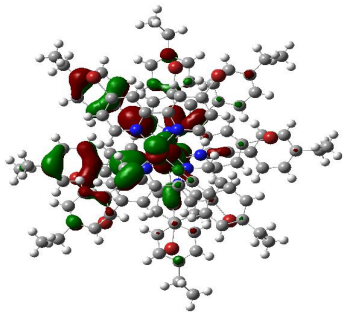

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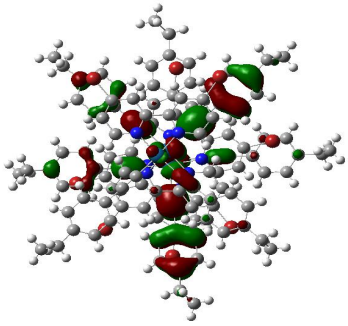

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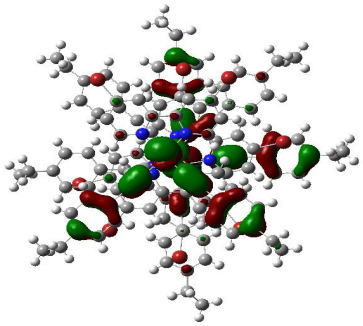

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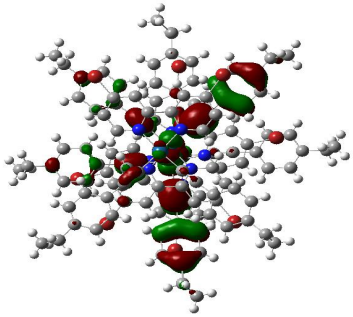
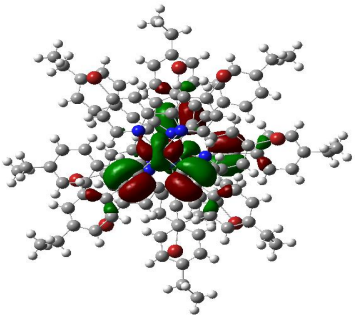


HOMO-8



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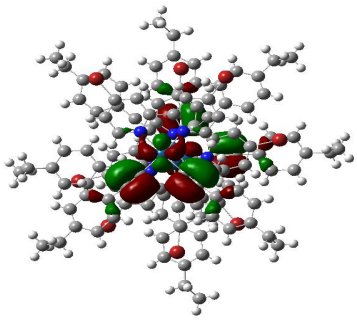
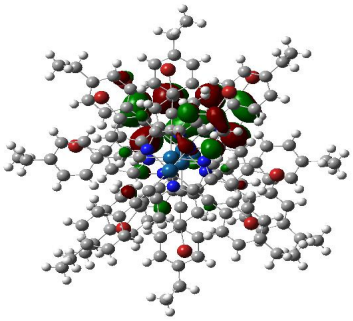


HOMO-10

**Figure S20.** Plots of the frontier molecular orbitals involved in the absorption transition for four-molecule model of **1**·1/8($CH_2Cl_2$) (isovalue = 0.02).



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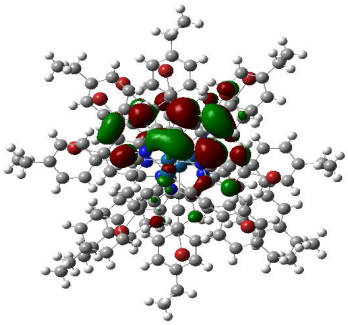

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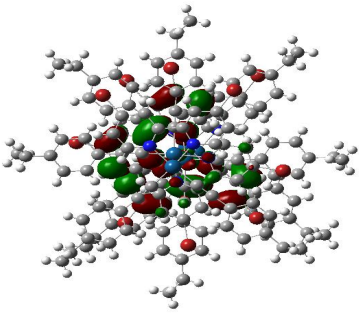

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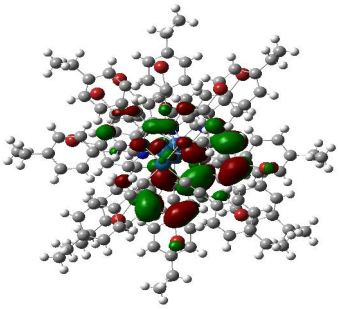

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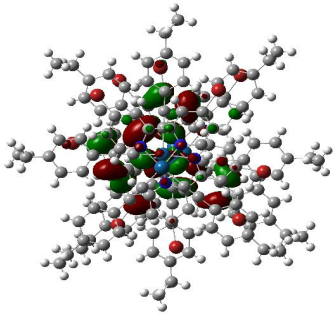
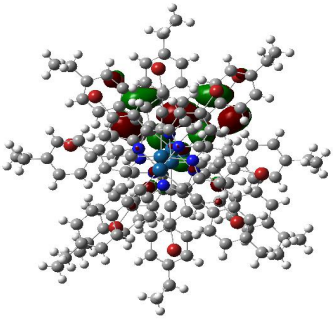
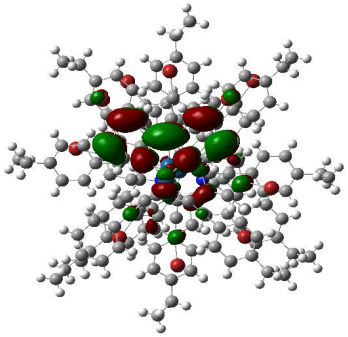


LUMO+2



LUMO+1



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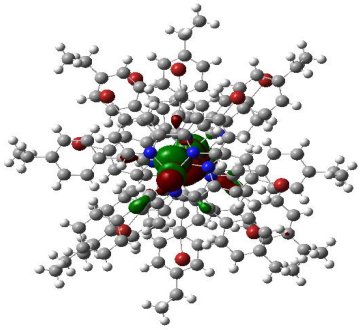
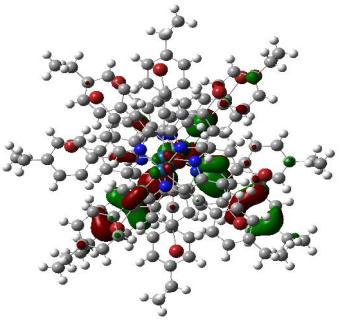
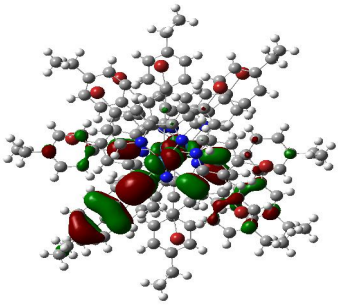


HOMO



HOMO-1



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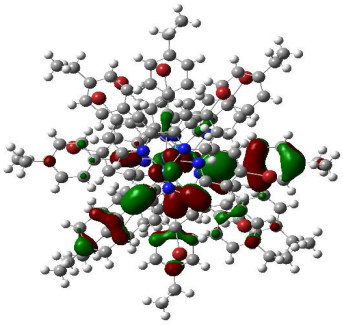
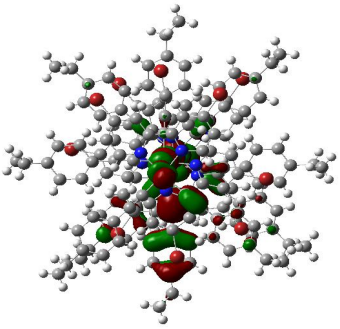


HOMO-3



HOMO-4

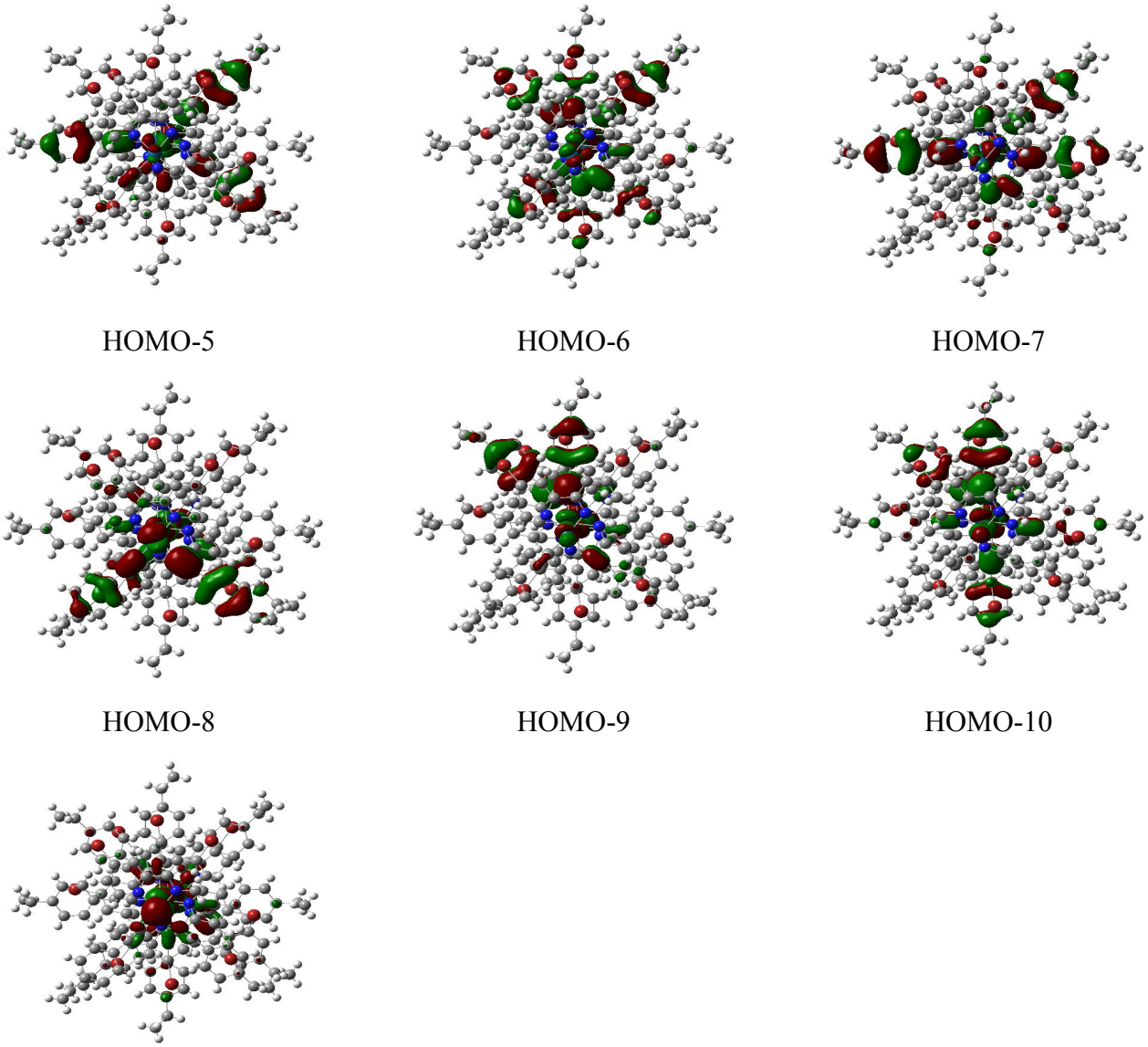



**Figure S21.** Plots of the frontier molecular orbitals involved in the absorption transition for five-molecule model of **1**·1/8($CH_2Cl_2$) (isovalue = 0.02).