

Supporting Information

Deciphering the Photophysical Role of Conjugated Diyne in Butadiynyl Fluorophores: Synthesis, Photophysical and Theoretical Study

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Experimental section

General: Melting points were recorded using Sigma melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on JASCO FT-IR-4100 spectrometer. ¹H (400 MHz, 500 MHz) and ¹³C (100 MHz, 125 MHz) NMR spectra were recorded on Bruker Avance 400 spectrometer and Bruker Avance 500 spectrometer respectively. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to chloroform. In the ¹³C NMR spectra, the nature of the carbons (C, CH, CH₂ or CH₃) was determined by recording the DEPT-135 experiment and is given in parentheses. High resolution mass measurements were carried out using Micromass Q-ToF ESI instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) were performed on glass plates (7.5 x 2.5 and 7.5 x 5.0 cm) coated with Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F₂₄₅ silica plates and various combinations of ethyl acetate and hexanes were used as eluent. Visualization of spots was accomplished by exposure to iodine vapor. All compounds were purified using silica gel [Acme's silica gel (100-200 mesh)] column chromatography. All small-scale dry reactions were carried out using standard syringe septum technique. Dry THF was obtained by distillation over sodium-benzophenone ketyl. Dry dichloromethane was prepared by distilling over calcium hydride. Coupling reactions were carried out using Sineo microwave oven (Sineo Microwave Chemistry Technology (China) Co., Ltd.).

For the photophysical studies, all the solvents used were of spectroscopic grade. The stock solution (10^{-3} M) for all the derivatives **1aa-1cd** was prepared in CH_2Cl_2 . The solutions in all other solvents (10^{-5} M) were prepared by evaporating the CH_2Cl_2 from the desired amount of the stock by gentle purging of nitrogen gas and then adding it with the solvent of interest. Absorption spectra were collected with a Jasco V-650 UV-vis Spectrometer. Fluorescence measurements were carried out with Horiba Jobin–Yvon FluoroMax-4 spectrofluorometer, with a 450 W xenon lamp as light source. The emission spectra were recorded with slit widths of 5/5 nm. Fluorescence lifetime experiment was carried out using a Horiba Jobin Yvon TCSPC lifetime instrument in a time-correlated, single-photon counting arrangement. 370 nm nano-LED was used as light source. The pulse repetition rate was set to 1 MHz and the instrumental full width half maximum of the 370 nm LED, including the detector response was around 800 ps. The instrument response function was collected using a scatterer (Ludox AS40 colloidal silica). The decay data were analyzed using IBH software. A value of χ^2 , $0.99 \leq \chi^2 \leq 1.3$ was considered as a good fit which was further judged by the symmetrical distribution of the residuals. The fluorescence quantum yield of fluorophore **1cd** was measured in various solvents using the following equation.¹

$$\phi_{\text{unk}} = \phi_{\text{std}} \times (F_{\text{unk}}/F_{\text{std}}) \times (A_{\text{std}}/A_{\text{unk}}) \times (n_{\text{unk}}^2/n_{\text{std}}^2) \times (q_{\text{std}}/q_{\text{unk}})$$

(unk: unknown; std: standard); where, F_{unk} , F_{std} correspond to the integrated intensities under the corrected emission spectra, A_{unk} , A_{std} correspond to the optical densities of the solutions, n_{unk} , n_{std} are refractive indices of the solvents used and q_{std} and q_{unk} are the excitation light intensities at the excitation wavelengths taken from the lamp profile of the fluorometer. The fluorescence quantum yield was measured relative to quinine sulphate ($\phi_f = 0.546$ in 1N H_2SO_4).²

All computational works were performed using Gaussian 03 program package. Optimization of ground state geometries of all the fluorophores were performed without any symmetry constraints at the DFT level with B3LYP hybrid functional using 6-31g* basis set. Vibrational analyses were carried out on the optimized geometry to confirm the structure.

The excitation energies and oscillator strengths for the first three singlet vertical transitions were achieved by TD-DFT calculations using the same basis set as for the ground state and using the same level of theory. 6-31g* basis set was used as a compromise between accuracy and CPU time. Origin 8 software was used for the Gaussian and Lorentzian curve fitting of emission spectra.

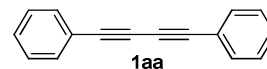
General procedure for the preparation of symmetrical 1,3-diynes (1aa-cc):

To a magnetically stirred solution of alkyne (1 mmol), Cu(OAc)₂·H₂O (10 mol%) in CH₂Cl₂ inside a microwave oven, piperidine (1 mmol) was added. The round bottom flask was fitted with condenser and the mixture was then stirred for 10 min in open atmosphere at rt using 400W microwave. The mixture was then concentrated under reduced pressure and purified on a silica gel column using ethyl acetate-hexane as eluent.

1,4-diphenylbuta-1,3-diyne (1aa):

Hexane was used as eluent to give the product as a white solid (99%).

Physical appearance: white solid.



R_f: 0.8 (Hexane)

m.p.: 87-89 °C (ref.³ m.p. 88-89 °C, ref.⁴ m.p. 86-87 °C)

IR (neat): 3050, 2924, 2852, 2147, 1591, 1481, 1436, 912, 684, 523 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.60-7.55 (m, 4H), 7.45-7.35 (m, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 132.63 (4 x CH), 129.34 (2 x CH), 128.56

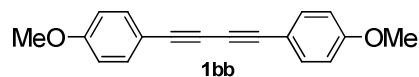
(4 x CH), 121.92 (2 x C), 81.70 (2 x C), 74.06 (2 x C).

HRMS (ESI, M+K⁺): m/z calcd. for C₁₆H₁₀K 241.0420, found 241.0416.

1,4-bis(4-methoxyphenyl)buta-1,3-diyne (1bb):

Ethyl acetate-hexane (1:49) was used as eluent to yield the diyne as a white solid (98%).

Physical appearance: white solid.



R_f: 0.6 (1:49, Ethyl acetate:Hexane)

m.p.: 140-142 °C (ref.³ m.p. 140-141 °C, ref.⁴ m.p. 143-144 °C)

IR (neat): 2970, 2918, 2842, 2134, 1596, 1564, 1462, 1109, 1019, 831, 689, 533 cm⁻¹.

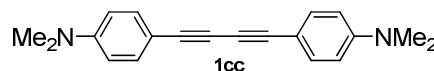
¹H NMR (400 MHz, CDCl₃): δ 7.46 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃, DEPT) δ 160.40 (2 x C), 134.19 (4 x CH), 114.29 (4 x CH), 114.12 (2 x C), 81.38 (2 x C), 73.10 (2 x C), 55.49 (2 x CH₃).

HRMS (ESI, M+H⁺): *m/z* calcd. for C₁₈H₁₅O₂ 263.1072, found 263.1075.

1,4-bis(4-N,N-dimethylaminophenyl)buta-1,3-diyne (1cc):

Use of ethyl acetate-hexane (1:19) as eluent furnished the product as a light brown solid (85%).



Physical appearance: light yellow solid.

Rf: 0.5 (1:19, Ethyl acetate:Hexane)

m.p.: 236-238 °C (ref.⁵ m.p. 235-238 °C)

IR (neat): 2923, 2853, 2810, 2121, 1601, 1514, 1359, 1166, 811, 526 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, *J* = 8.7 Hz, 4H), 6.62 (d, *J* = 8.7 Hz, 4H), 2.99 (s, 12H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 150.40 (2 x C), 133.74 (4 x CH), 111.82 (4 x CH), 108.70 (2 x C), 82.49 (2 x C), 72.73 (2 x C), 40.27 (4 x CH₃).

HRMS (ESI, M+H⁺): *m/z* calcd. for C₂₀H₂₁N₂ 289.1705, found 289.1701.

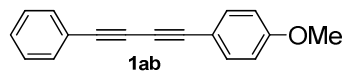
General procedure for the preparation of unsymmetrical 1,3-diynes (1ab-cd):

To a magnetically stirred solution of alkyne X (1 mmol), alkyne Y (5 mmol), Cu(OAc)₂.H₂O (10 mol %) in CH₂Cl₂ inside a microwave oven, piperidine (3 mmol) was added. The round bottom flask was fitted with condenser and the mixture was then stirred for 15 min in open atmosphere at rt using 400W microwave. The mixture was then concentrated under reduced pressure and purified on a silica gel column using ethyl acetate-hexane as eluent.

1-methoxy-4(4-phenylbuta-1,3-diynyl)benzene (1ab):

ethyl acetate-hexane (1:99) as eluent to afford the diyne as a white solid (75%).

Physical appearance: white solid.



R_f: 0.7 (1:99, Ethyl acetate:Hexane)

m.p.: 96-98 °C (ref.³ m.p. 95-96 °C, ref.⁴ m.p. 97-98 °C)

IR (neat): 3059, 2954, 2206, 2145, 1581, 1458, 1242, 1157, 1018, 822, 517 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.55-7.45 (m, 4H), 7.40-7.30 (m, 3H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H).

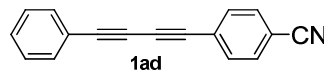
¹³C NMR (100 MHz, CDCl₃, DEPT): δ 160.49 (1 x C), 134.24 (2 x CH), 132.54 (2 x CH), 129.15 (1 x CH), 128.53 (2 x CH), 122.11 (1 x C), 114.28 (2 x CH), 113.78 (1 x C), 81.97 (1 x C), 81.15 (1 x C), 74.33 (1 x C), 72.88 (1 x C), 55.43 (1 x CH₃).

HRMS (ESI, M+H⁺): m/z calcd. for C₁₇H₁₃O 233.0966, found 233.0975.

4-(4-phenylbuta-1,3-diyne)benzonitrile (1ad):

ethyl acetate-hexane (1:24) as eluent to afford the diyne as a white solid (66%).

Physical appearance: white solid.



R_f: 0.5 (1:24, Ethyl acetate:Hexane)

m.p.: 197-198 °C

IR (neat): 3070, 2924, 2326, 2210, 2137, 1597, 1481, 837, 760, 544 cm⁻¹.

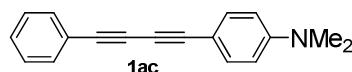
¹H NMR (400 MHz, CDCl₃): δ 7.65-7.58 (m, 4H), 7.55-7.50 (m, 2H), 7.45-7.30 (m, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 133.06 (2 x CH), 132.78 (2 x CH), 132.24 (2 x CH), 129.88 (1 x CH), 128.67 (2 x CH), 127.00 (1 x C), 121.33 (1 x C), 118.37 (1 x C), 112.54 (1 x C), 84.10 (1 x C), 79.46 (1 x C), 78.30 (1 x C), 73.38 (1 x C).

HRMS (ESI, M+Na⁺): m/z calcd. for C₁₇H₉NNa 250.0633, found 250.0621.

N,N-dimethyl-4-(4-phenylbuta-1,3-diyne)benzeneamine (1ac):

Use of ethylacetate-hexane (1:24) as eluent furnished the diyne **1ac** as a light brown solid (74%).



Physical appearance: brown solid.

R_f: 0.5, (1:24, Ethyl acetate:Hexane)

m.p.: 110-112 °C (ref.⁶ m.p. 113 °C)

IR (neat): 2903, 2850, 2815, 2204, 2138, 1596, 1522, 1483, 1439, 1373, 1231, 1167, 813, 755, 690, 526 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.55 -7.50 (m, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.35-7.30 (m, 3H), 6.64 (d, *J* = 8.8 Hz), 3.00 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 150.70 (1 x C), 133.96 (2 x CH), 132.45 (2 x CH), 128.86 (1 x CH), 128.45 (2 x CH), 122.51 (1 x C), 111.79 (2 x CH), 107.96 (1 x CH), 83.62 (1 x C), 80.89 (1 x C), 74.83 (1 x C), 72.20 (1 x C), 40.21 (2 x CH₃).

HRMS (ESI, M+H⁺): m/z calcd. for C₁₈H₁₆N 246.1283, found 246.1279.

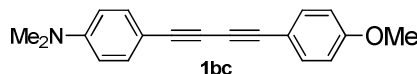
4-(4-(4-methoxyphenyl)buta-1,3-diynyl)-N,N-dimethylbenzenamine (1bc):

Use of dichloromethane-hexane (1:4) as eluent yielded a white solid (78%).

Physical appearance: white solid.

R_f: 0.4, (1:4, Dichloromethane:Hexane)

m.p.: 156-158 °C



IR (neat): 2922, 2856, 2202, 2129, 1601, 1506, 1251, 1168, 837, 818, 539 cm⁻¹.

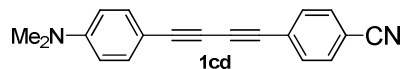
¹H NMR (500 MHz, CDCl₃): δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.00 (s, 6H).

¹³C NMR (125 MHz, CDCl₃, DEPT): δ 160.16 (1 x C), 150.63 (1 x C), 134.05 (2 x CH), 133.89 (2 x CH), 114.49 (1 x C), 114.22 (2 x CH), 111.82 (2 x CH), 108.29 (1 x C), 82.95 (1 x C), 81.30 (1 x C), 73.55 (1 x C), 72.37 (1 x C), 55.47 (1 x CH₃), 40.24 (2 x CH₃).

HRMS (ESI, M+H⁺): m/z calcd. for C₁₉H₁₈NO 276.1338, found 276.1396.

4-(4-(4-dimethylamino)phenyl)buta-1,3-diynyl)benzonitrile (1cd):

Dichloromethane- hexane (1:4) was used as eluent to furnish a yellow solid (73%).



Physical appearance: yellow solid.

R_f: 0.4, (1:4, Dichloromethane:Hexane)

m.p.: 178-180 °C

IR (neat): 2920, 2851, 2197, 2128, 1599, 1524, 1367, 1175, 824 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ 7.60-7.50 (m, 4H), 7.41 (d, *J* = 9 Hz, 2H), 6.61 (d, *J* = 9 Hz, 2H), 3.01 (s, 6H).

¹³C NMR (125 MHz, CDCl₃, DEPT): δ 150.98 (1 x C), 134.14 (2 x CH), 132.77 (2 x CH), 132.13 (2x CH), 127.61 (1x C), 118.55 (1 x C), 111.73 (2 x CH), 107.05 (1 x C), 86.46 (1 x C), 79.42 (1 x C), 78.99 (1 x C), 71.85 (1 x C), 40.14 (2 x CH₃).

HRMS (ESI, M+H⁺): m/z calcd. for C₁₉H₁₅N₂ 271.1235, found 271.1239.

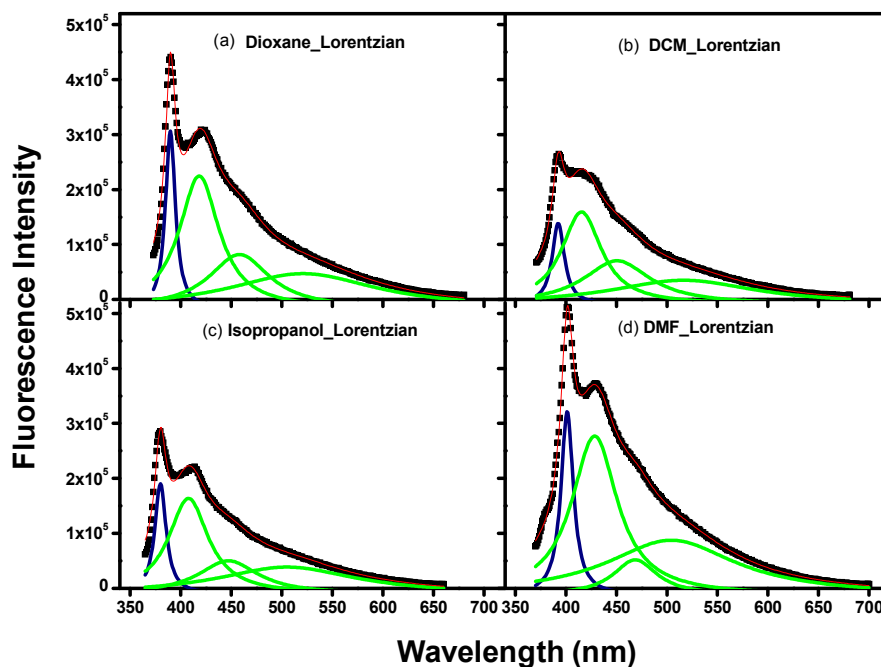


Figure S1. Lorentzian fitting of emission spectra of **1cc** (blue peak indicates Raman scattering)

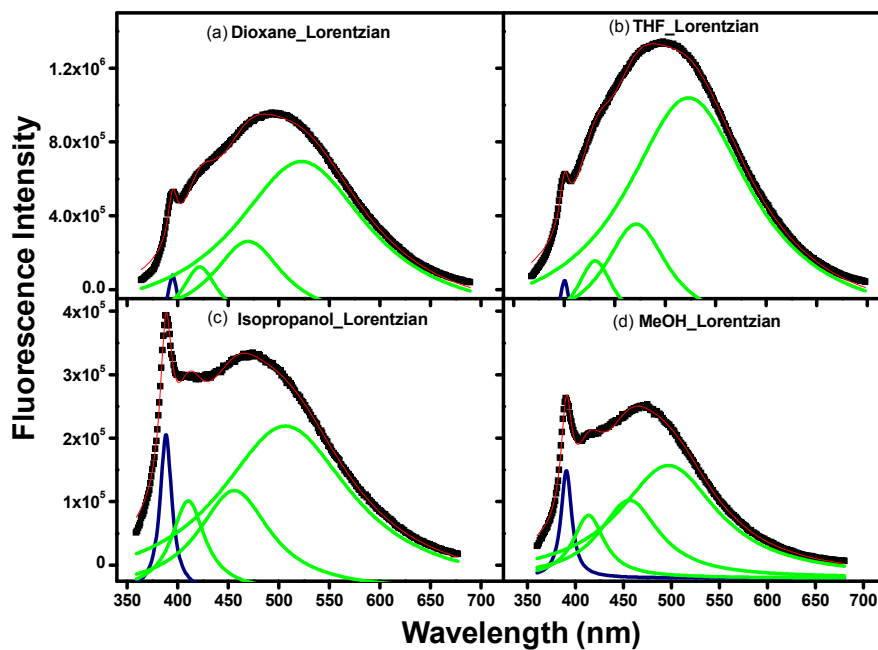


Figure S2. Lorentzian fitting of emission spectra of **1ac** (blue peak indicates Raman scattering)

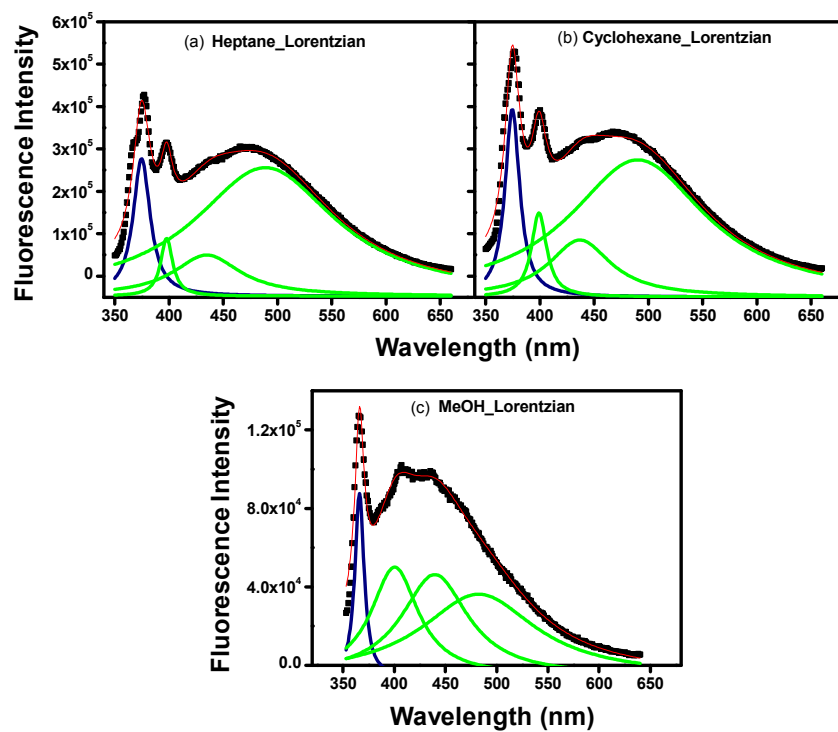


Figure S3. Lorentzian fitting of emission spectra of **1bc** (blue peak indicates Raman scattering)

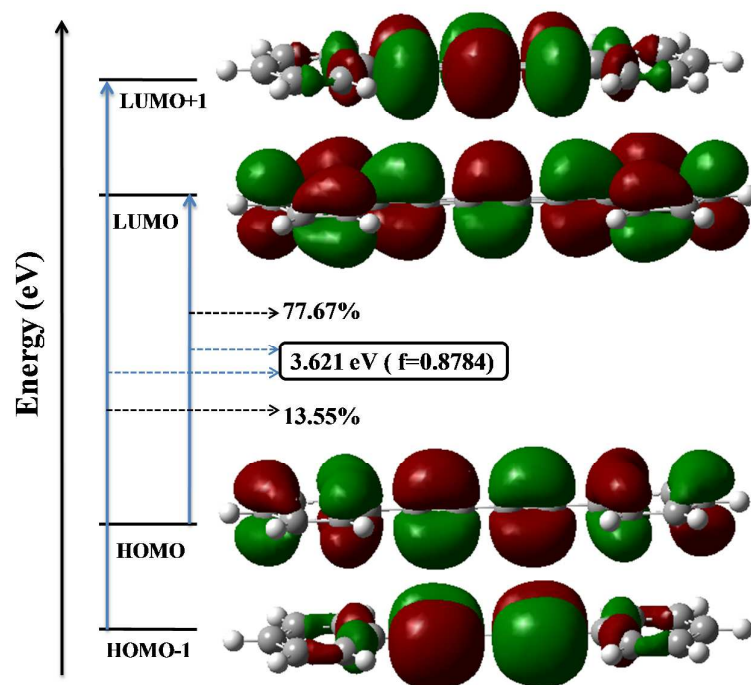


Figure S4. Frontier orbitals of **1aa** for the first singlet vertical transition

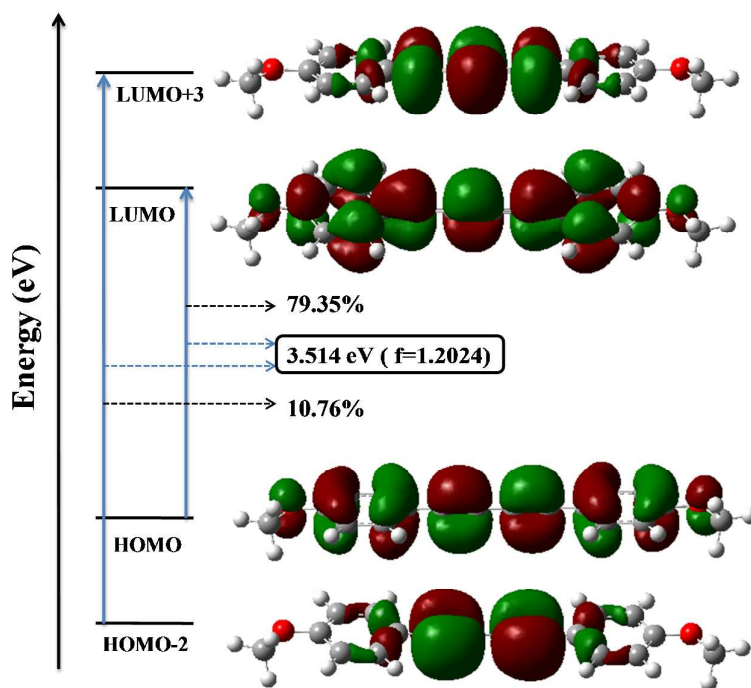


Figure S5. Frontier orbitals of **1bb** for the first singlet vertical transition

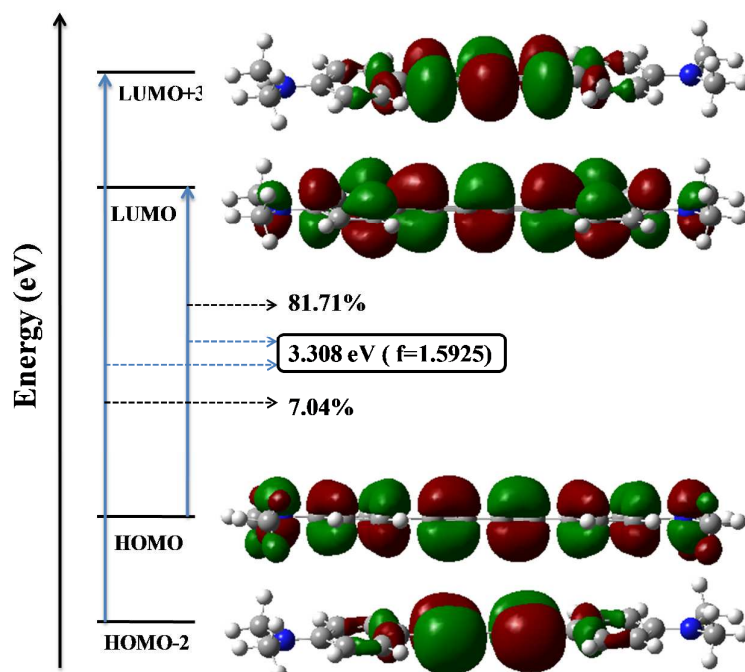


Figure S6. Frontier orbitals of **1cc** for the first singlet vertical transition

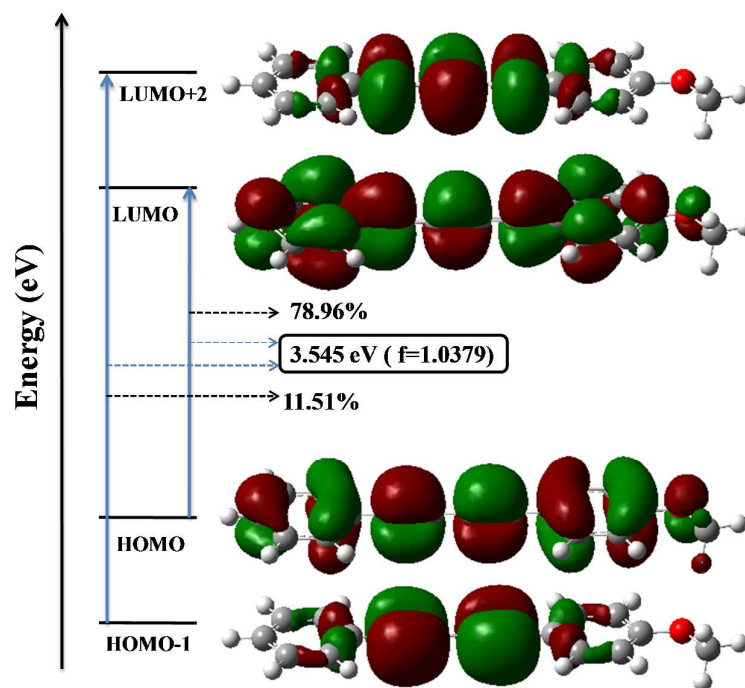


Figure S7. Frontier orbitals of **1ab** for the first singlet vertical transition

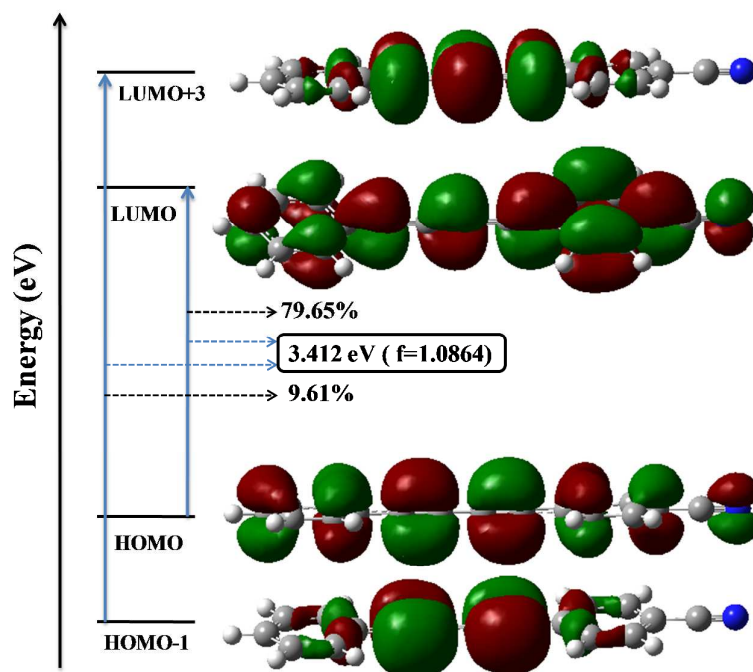


Figure S8. Frontier orbitals of **1ad** for the first singlet vertical transition

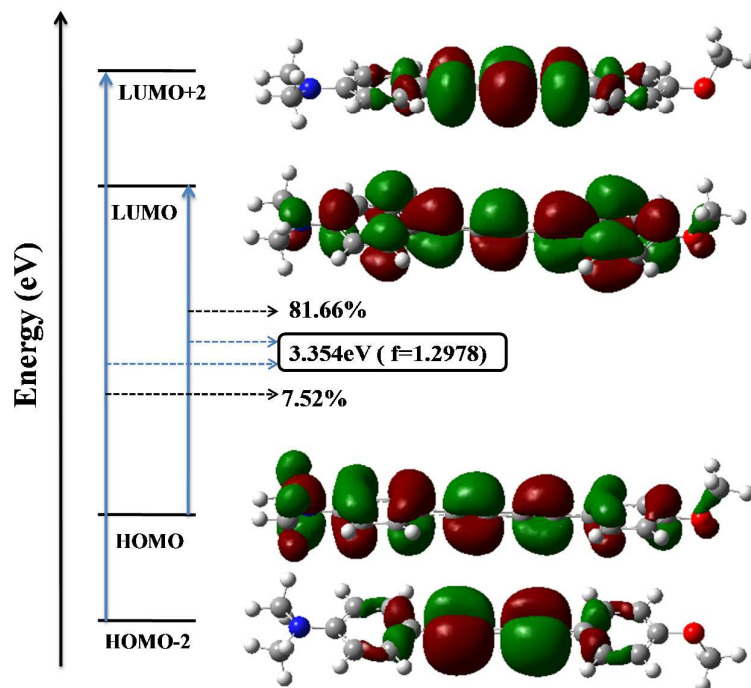


Figure S9. Frontier orbitals of **1bc** for the first singlet vertical transition

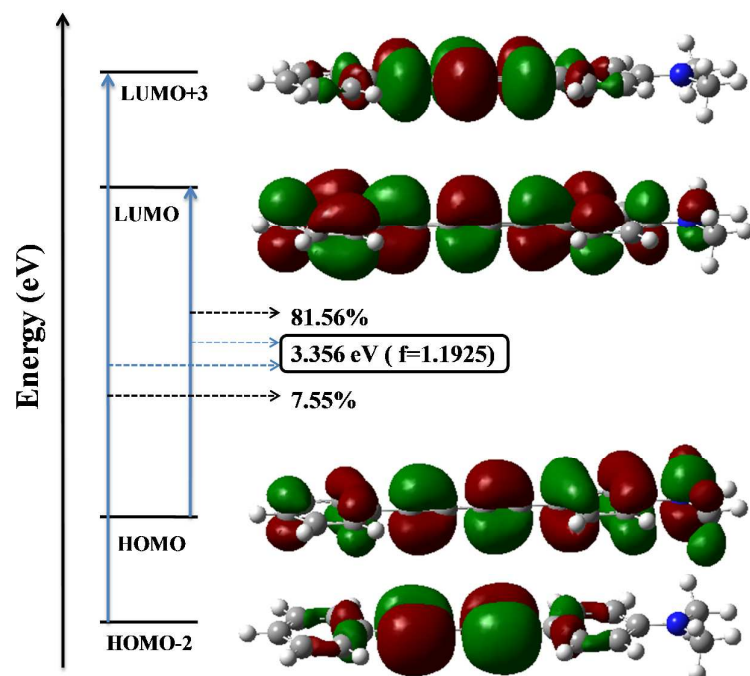


Figure S10. Frontier orbitals of **1ac** for the first singlet vertical transition

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