# Computational Studies of the Electronic Absorption Spectrum of [(2,2′;6′,2′′-Terpyridine)-Pt(II)-OH] [7,7,8,8-Tetracyanoquinodimethane] Complex

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# 1 Supplementary information

## 1.1 Cartesian coordinates (in Å) for neutral TCNQ

```
20

C     1.2400927    0.6859173    0.0000000
C     1.2400927   -0.6859173    0.0000000
C     0.0000000   -1.4319218    0.0000000
C    -1.2400927   -0.6859173    0.0000000
C    -1.2400927    0.6859173    0.0000000
C     0.0000000    1.4319218    0.0000000
H     2.1938251    1.2376396    0.0000000
H     2.1938251   -1.2376396    0.0000000
H    -2.1938251   -1.2376396    0.0000000
H    -2.1938251    1.2376396    0.0000000
C     0.0000000   -2.8427295    0.0000000
C     0.0000000    2.8427295    0.0000000
C    -1.2150973   -3.5952549    0.0000000
N    -2.2159900   -4.2132522    0.0000000
C     1.2150973   -3.5952549    0.0000000
N     2.2159900   -4.2132522    0.0000000
C    -1.2150973    3.5952549    0.0000000
N    -2.2159900    4.2132522    0.0000000
C     1.2150973    3.5952549    0.0000000
N     2.2159900    4.2132522    0.0000000
```

## 1.2 Cartesian coordinates (in Å) for the $TCNQ^{-}$ anion

```
20

C     1.2095462    0.6847520    0.0000000
C     1.2095462   -0.6847520    0.0000000
C     0.0000000   -1.4304132    0.0000000
C    -1.2095462   -0.6847520    0.0000000
C    -1.2095462    0.6847520    0.0000000
C     0.0000000    1.4304132    0.0000000
H     2.1526891    1.2171418    0.0000000
H     2.1526891   -1.2171418    0.0000000
H    -2.1526891   -1.2171418    0.0000000
H    -2.1526891    1.2171418    0.0000000
C     0.0000000   -2.8567760    0.0000000
C     0.0000000    2.8567760    0.0000000
C    -1.2020754   -3.5966604    0.0000000
N    -2.1967164   -4.1926871    0.0000000
```

| | | | |
|---|---|---|---|
| C | 1.2020754 | -3.5966604 | 0.0000000 |
| N | 2.1967164 | -4.1926871 | 0.0000000 |
| C | -1.2020754 | 3.5966604 | 0.0000000 |
| N | -2.1967164 | 4.1926871 | 0.0000000 |
| C | 1.2020754 | 3.5966604 | 0.0000000 |
| N | 2.1967164 | 4.1926871 | 0.0000000 |

## 1.3 Cartesian coordinates (in Å) for the $TCNQ^{2-}$ dianion

20

| | | | |
|---|---|---|---|
| C | 1.1899321 | 0.6945068 | 0.0000000 |
| C | 1.1899321 | -0.6945068 | 0.0000000 |
| C | 0.0000000 | -1.4446721 | 0.0000000 |
| C | -1.1899321 | -0.6945068 | 0.0000000 |
| C | -1.1899321 | 0.6945068 | 0.0000000 |
| C | 0.0000000 | 1.4446721 | 0.0000000 |
| H | 2.1403903 | 1.2175855 | 0.0000000 |
| H | 2.1403903 | -1.2175855 | 0.0000000 |
| H | -2.1403903 | -1.2175855 | 0.0000000 |
| H | -2.1403903 | 1.2175855 | 0.0000000 |
| C | 0.0000000 | -2.9154481 | 0.0000000 |
| C | 0.0000000 | 2.9154481 | 0.0000000 |
| C | -1.1933204 | -3.6483095 | 0.0000000 |
| N | -2.1957013 | -4.2480263 | 0.0000000 |
| C | 1.1933204 | -3.6483095 | 0.0000000 |
| N | 2.1957013 | -4.2480263 | 0.0000000 |
| C | -1.1933204 | 3.6483095 | 0.0000000 |
| N | -2.1957013 | 4.2480263 | 0.0000000 |
| C | 1.1933204 | 3.6483095 | 0.0000000 |
| N | 2.1957013 | 4.2480263 | 0.0000000 |

## 1.4 Cartesian coordinates (in Å) for $[Pt(trpy)OH]^{+}$

32

| | | | |
|---|---|---|---|
| C | 0.5571098 | 3.7100844 | 0.0000000 |
| C | 0.4755234 | 2.3258956 | 0.0000000 |
| N | 1.6176970 | 1.5741225 | 0.0000000 |
| C | 2.8191786 | 2.1548991 | 0.0000000 |
| C | 2.9498271 | 3.5364047 | 0.0000000 |
| C | 1.8058544 | 4.3211064 | 0.0000000 |
| C | -0.7832719 | 1.5543281 | 0.0000000 |
| N | -0.5873922 | 0.2179296 | 0.0000000 |
| C | -1.5865504 | -0.6855365 | 0.0000000 |

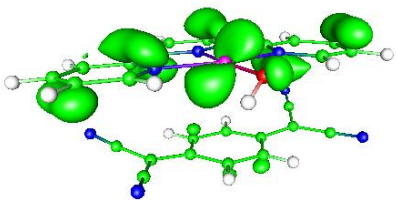
| | | | |
|---|---|---|---|
| C | -2.9021872 | -0.2358297 | 0.0000000 |
| C | -3.1418273 | 1.1344884 | 0.0000000 |
| C | -2.0848791 | 2.0403333 | 0.0000000 |
| Pt | 1.2512485 | -0.4225572 | 0.0000000 |
| O | 3.1786456 | -0.8296499 | 0.0000000 |
| C | -1.0976772 | -2.0758479 | 0.0000000 |
| C | -1.9243719 | -3.1904983 | 0.0000000 |
| C | -1.3687123 | -4.4623380 | 0.0000000 |
| C | 0.0120771 | -4.5940401 | 0.0000000 |
| C | 0.7938844 | -3.4502239 | 0.0000000 |
| N | 0.2655755 | -2.2214205 | 0.0000000 |
| H | -2.0070890 | -5.3356810 | 0.0000000 |
| H | -4.1597952 | 1.4998088 | 0.0000000 |
| H | 1.8796155 | 5.4006242 | 0.0000000 |
| H | 0.4880806 | -5.5646723 | 0.0000000 |
| H | 1.8726632 | -3.5075269 | 0.0000000 |
| H | -2.9977205 | -3.0649480 | 0.0000000 |
| H | -3.7283528 | -0.9321264 | 0.0000000 |
| H | -2.2796233 | 3.1032574 | 0.0000000 |
| H | -0.3432704 | 4.3074678 | 0.0000000 |
| H | 3.9363716 | 3.9784534 | 0.0000000 |
| H | 3.6594378 | 1.4713430 | 0.0000000 |
| H | 3.4299306 | -1.7576498 | 0.0000000 |

## 1.5 Cartesian coordinates (in Å) for [Pt(trpy)OH]TCNQ

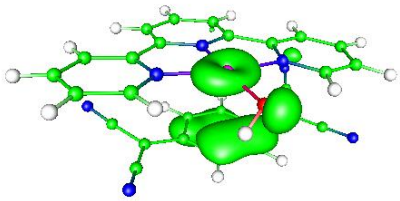
52

| | | | |
|---|---|---|---|
| C | 0.3397025 | 0.8792922 | -3.4623254 |
| C | 0.2182119 | 1.0223101 | -2.0889333 |
| N | 1.3279848 | 1.2450057 | -1.3216214 |
| C | 2.5378107 | 1.3164491 | -1.8788709 |
| C | 2.7101997 | 1.1718140 | -3.2473618 |
| C | 1.5978378 | 0.9536430 | -4.0463105 |
| C | -1.0475647 | 0.9090050 | -1.3421955 |
| N | -0.8920827 | 1.0568878 | -0.0117299 |
| C | -1.8906288 | 0.9277918 | 0.8825829 |
| C | -3.1689984 | 0.6331937 | 0.4242008 |
| C | -3.3710981 | 0.5015290 | -0.9463107 |
| C | -2.3152019 | 0.6381709 | -1.8418362 |
| Pt | 0.9110969 | 1.3651339 | 0.6604308 |
| O | 2.8072368 | 1.6467193 | 1.1759862 |
| C | -1.4431227 | 1.1210638 | 2.2717589 |
| C | -2.2807190 | 1.0556560 | 3.3757526 |
| C | -1.7574115 | 1.2628206 | 4.6442050 |

| | | | |
|---|---|---|---|
| C | -0.4071812 | 1.5434639 | 4.7845052 |
| C | 0.3876594 | 1.5898126 | 3.6510119 |
| N | -0.1065207 | 1.3811599 | 2.4290535 |
| N | -3.5126131 | -1.9394361 | 2.5982694 |
| C | -2.3886512 | -2.0812017 | 2.3501708 |
| C | -1.0259376 | -2.1642237 | 2.0046417 |
| C | -0.0925016 | -1.9083749 | 3.0306829 |
| N | 0.6852458 | -1.6524253 | 3.8502682 |
| C | -0.6178798 | -2.3517454 | 0.6530043 |
| C | 0.7505784 | -2.2938186 | 0.2732044 |
| C | 1.1304009 | -2.3619352 | -1.0399935 |
| C | 0.1727366 | -2.4733727 | -2.0828440 |
| C | -1.1895387 | -2.5971029 | -1.6973431 |
| C | -1.5682282 | -2.5464547 | -0.3840335 |
| C | 0.5492870 | -2.4050927 | -3.4539676 |
| C | 1.8985054 | -2.2972596 | -3.8488666 |
| N | 3.0087358 | -2.1635332 | -4.1513102 |
| C | -0.4253750 | -2.2626145 | -4.4637341 |
| N | -1.2483773 | -2.0777258 | -5.2586025 |
| H | -2.4003746 | 1.1947293 | 5.5113489 |
| H | -4.3587798 | 0.2654500 | -1.3183185 |
| H | 1.7075531 | 0.8065727 | -5.1118494 |
| H | 0.0409245 | 1.7016320 | 5.7549201 |
| H | 1.4471439 | 1.7916102 | 3.7024582 |
| H | -3.3233688 | 0.8089190 | 3.2459677 |
| H | -3.9797522 | 0.4770351 | 1.1194812 |
| H | -2.4715514 | 0.4994782 | -2.9019434 |
| H | -0.5316095 | 0.6703924 | -4.0660148 |
| H | 3.7047127 | 1.2019150 | -3.6681791 |
| H | 3.3502602 | 1.4752172 | -1.1812541 |
| H | 3.0237395 | 1.2557221 | 2.0287769 |
| H | 2.1804864 | -2.2916175 | -1.2943136 |
| H | 1.5047269 | -2.1676835 | 1.0389806 |
| H | -2.6161075 | -2.6372539 | -0.1280510 |
| H | -1.9430376 | -2.7250270 | -2.4646182 |



(a)



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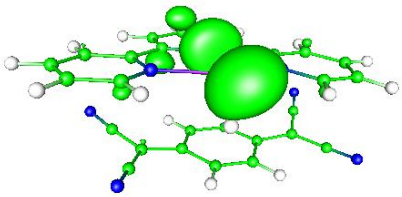

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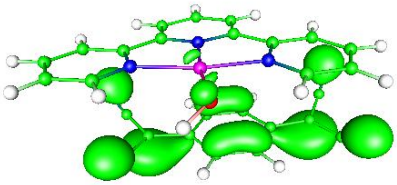

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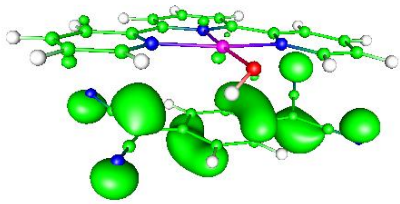
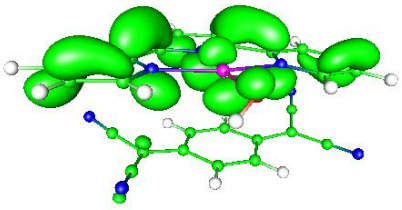


(e)



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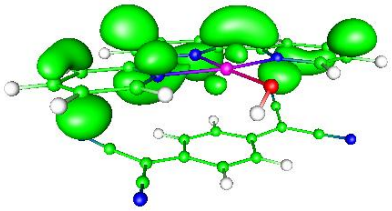
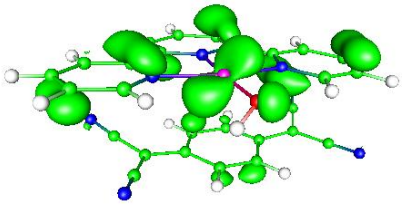


(g)

Figure S1: The electron density of the frontier orbitals of the $\alpha$ electrons for [Pt(trpy)OH]TCNQ: (a) $123a_{\alpha}$, (b) $124a_{\alpha}$, (c) $125a_{\alpha}$, (d) $126_{\alpha}$, (e) $127a_{\alpha}$ = $(HOMO)_{\alpha}$ = (HOMO), (f) $128a_{\alpha}$,and (g) $129a_{\alpha}$



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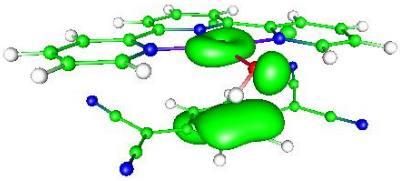
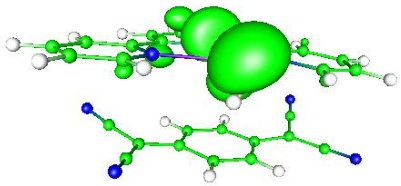


(k)



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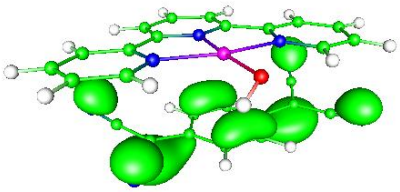

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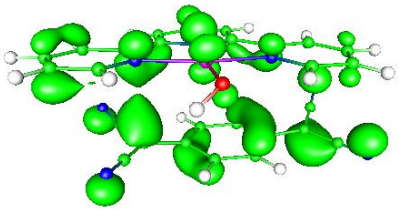

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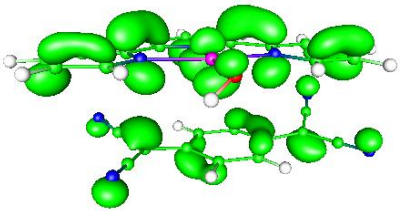
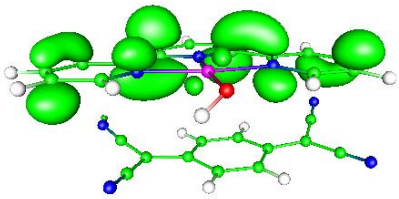
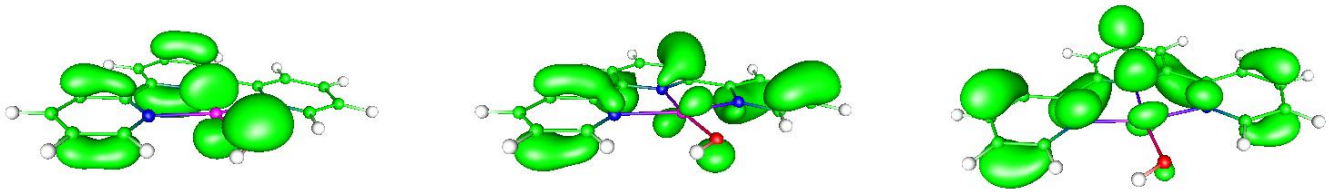


(o)

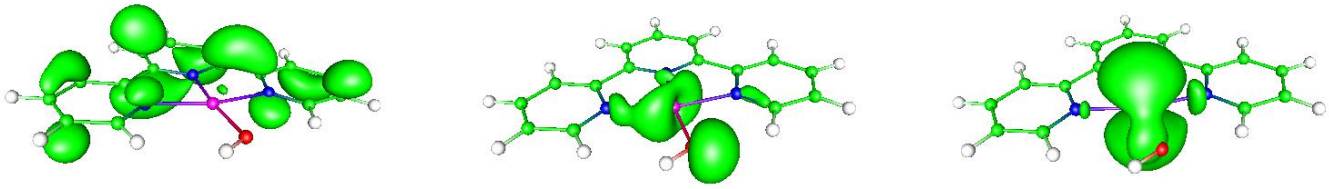


(p)

Figure S2: The electron density of the frontier orbitals of the $\beta$ electrons for [Pt(trpy)OH]TCNQ: (a) 123a$_\beta$, (b) 124a$_\beta$, (c) 125a$_\beta$, (d) 126a$_\beta$ = (HOMO)$_\beta$, (e) 127a$_\beta$, (f) 128a$_\beta$,and (g) 129a$_\beta$



(s) (t) (u)



(v) (w) (x)

Figure S3: The electron density of the frontier orbitals for $[Pt(trpy)OH]^+$: (a) 12a″, (b) 13a″ = (HOMO), (c) 14a″ = (LUMO), (d) 15a″, (e) 60a′, and (f) 61a′.

## 2 Population analysis

Mulliken population analysis were performed using the AOMix program based on the B3LYP/def2-TZVP calculations. Table S2 lists the atomic orbital (AO) contributions to the molecular orbitals (MO) of $[Pt(trpy)OH]^+$. Table S3 lists the AO contributions to the HOMO and LUMO of [Pt(trpy)OH]TCNQ. The charge-transfer nature of the HOMO-LUMO transition in [Pt(trpy)OH]TCNQ is reflected in the population analysis. The whole HOMO is practically located on the $[Pt(trpy)OH]^+$ part and the LUMO is on $[TCNQ]^-$.

Table S1: The lowest excitation energies (E in eV) and the corresponding wave length ($\lambda$ in nm) of the [Pt(trpy)OH]TCNQ complex calculated at the B3LYP/TZVP level and using the COSMO model to simulate solvent effects. The oscillator strengths (f) are also reported.

| State | E | $\lambda$ | f |
|---|---|---|---|
| 2A | 1.57 | 790 | 0.028 |
| 3A | 1.64 | 757 | 0.222 |
| 4A | 1.87 | 663 | 0.003 |
| 5A | 2.02 | 615 | 0.002 |
| 6A | 2.30 | 539 | 0.000 |
| 7A | 2.39 | 518 | 0.011 |
| 8A | 2.54 | 489 | 0.001 |
| 9A | 2.68 | 463 | 0.004 |
| 10A | 2.72 | 456 | 0.002 |
| 11A | 2.78 | 446 | 0.018 |
| 12A | 2.85 | 435 | 0.001 |
| 13A | 2.90 | 428 | 0.002 |
| 14A | 2.91 | 426 | 0.003 |
| 15A | 2.92 | 425 | 0.000 |
| 16A | 2.94 | 422 | 0.002 |
| 17A | 2.97 | 418 | 0.000 |
| 18A | 2.99 | 414 | 0.023 |
| 19A | 3.05 | 406 | 0.004 |
| 20A | 3.10 | 400 | 0.001 |
| 21A | 3.11 | 399 | 0.000 |

Table S2: Atomic orbital (AO) contributions to the molecular orbitals (MO) for $[Pt(trpy)OH]^+$ are given. The AO contributions given in (%) are rounded to the closest integer. For Pt, the AO contributions are given by orbital type, and for C, N, and O, the total AO contribution per atom is reported. The hydroxyl hydrogen is listed separately. All the other hydrogen atoms are added together. The atomic numbering is shown in Figure S4. Zero entries are represented by blanks. The AO contributions are obtained from a Mulliken population analysis at the B3LYP/def2-TZVP level.

| Atom/orbital | HOMO-1 | HOMO | LUMO | LUMO+1 |
|---|---|---|---|---|
| Pts | 19 | | | |
| Ptp | | 2 | 1 | |
| Ptd | 68 | 34 | 7 | 1 |
| O | 9 | 48 | 3 | |
| OH-hydrogen | | | | |
| N3 | | 1 | 1 | 4 |
| C4 | | | 4 | 7 |
| C5 | 2 | | 4 | 5 |
| C6 | | 1 | 2 | 1 |
| C7 | | 1 | 3 | 8 |
| N8 | | | 4 | 3 |
| C9 | | 3 | 5 | 9 |
| C10 | | 1 | 14 | 1 |
| C11 | | 3 | 8 | 5 |
| C12 | | | 1 | 19 |
| C13 | | 4 | 8 | 2 |
| C14 | | | 3 | 16 |
| C15 | | | 8 | 5 |
| C16 | | 1 | 2 | 3 |
| C17 | | 1 | 7 | 1 |
| C18 | | | 6 | 5 |
| C19 | 1 | 1 | 2 | |
| N20 | | | 7 | 3 |
| CH-hydrogen | | | | 1 |

Table S3: The AO contributions to the HOMO and $\alpha$LUMO orbitals of [Pt(trpy)OH]TCNQ are listed. The horizontal line approximately in the middle divides the complex into the $[Pt(trpy)OH]^+$ part (above) and the $TCNQ^-$ part (below). The AO contributions given in (%) are rounded to the closest integer. For Pt, the AO contributions are given by orbital type, and for C, N, and O, the total AO contribution per atom is reported. The hydroxyl hydrogen is listed separately. All the other hydrogen atoms are added together. The atomic numbering is shown in Figure S5. Zero entries are represented by blanks. The AO contributions are obtained from a Mulliken population analysis at the B3LYP/def2-TZVP level.

| Atom/orbital | HOMO | $\alpha$LUMO |
|---|---|---|
| Pt *s* | | |
| Pt *p* | | 1 |
| Pt *d* | | 6 |
| O | | 2 |
| OH-hydrogen | | |
| C1 | | 1 |
| C2 | | 5 |
| N3 | | 5 |
| C4 | | 2 |
| C5 | | 4 |
| C6 | | 5 |
| C7 | | 6 |
| N8 | | 14 |
| C9 | | 7 |
| C10 | | 1 |
| C11 | | 9 |
| C12 | | 2 |
| C15 | | 7 |
| C16 | 1 | 2 |
| C17 | | 6 |
| C18 | 1 | 5 |
| C19 | | 2 |
| N20 | | 6 |
| N21 | 6 | |
| C22 | 1 | |
| C23 | 16 | 1 |
| C24 | 1 | |
| N25 | 6 | |
| C26 | 8 | |
| C27 | 5 | 1 |
| C28 | 4 | |
| C29 | 8 | |
| C30 | 5 | |
| C31 | 5 | |
| C32 | 15 | |
| C33 | 1 | |
| N34 | 6 | |
| C35 | X | |
| N36 | 6 | |
| CH-hydrogen | | |

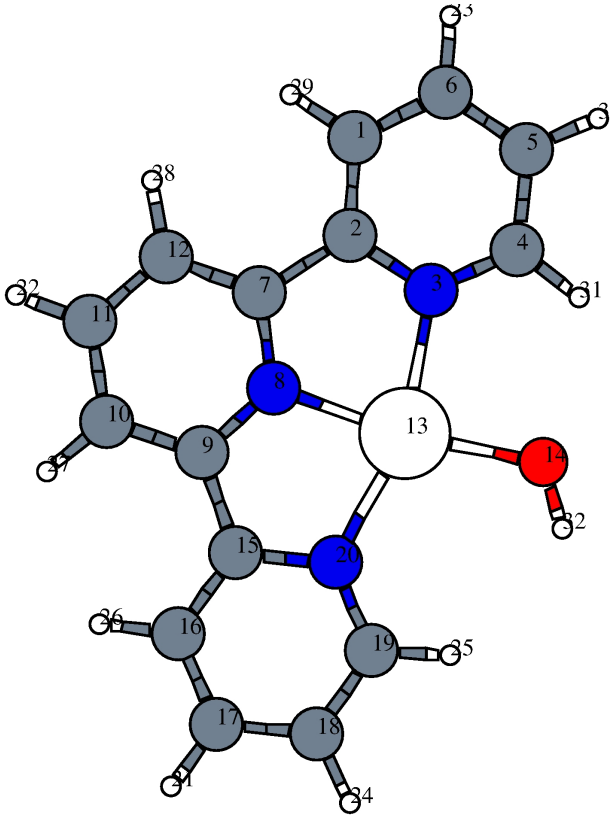



Figure 1: Numbering of atoms in $[Pt(trpy)OH]^{+}$, as referred to in Table S2.

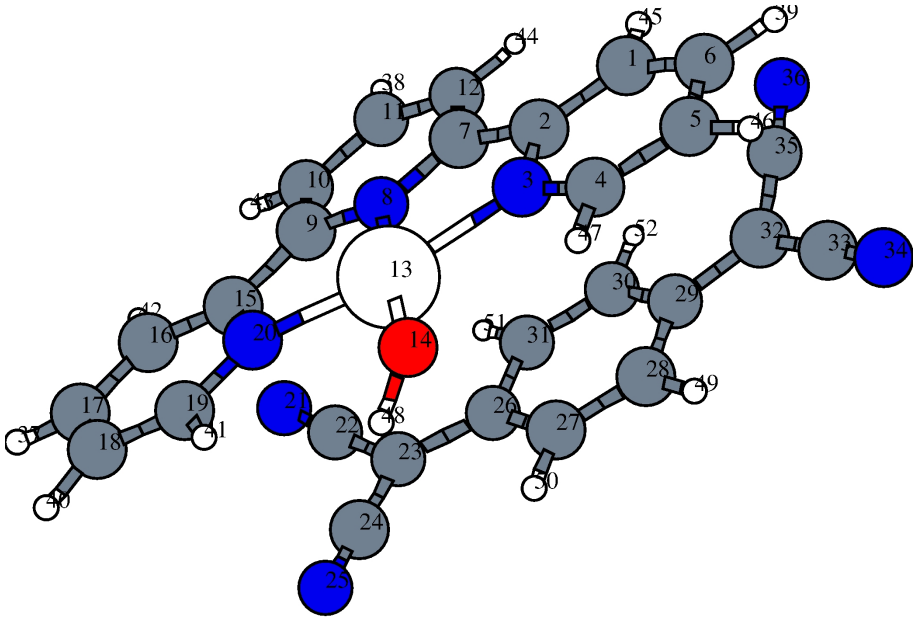



Figure 2: Numbering of atoms in [Pt(trpy)OH]TCNQ, as referred to in Table S3.