Electronic Supplementary Information for Dalton Transactions

Supporting Information

Self-Assembled Molecular Squares Containing Metal-Based Donor: Synthesis and Application in the Sensing of Nitro-aromatics

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General procedure. *cis*-(dppf)$PtCl_2$[1] and **3**[2] were prepared by literature procedure and *cis*-(dppf)$PdCl_2$ was purchased from Aldrich and used as such without purification. Metal based acceptors **1** and **2** were prepared from the corresponding chloride analogues [*cis*-(dppf)M)Cl_2] by treating with $AgCF_3SO_3$. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker 300 MHz machine. ^{1}H chemical shifts are reported relative to the residual protons of deuterated CD_3COCD_3 (2.05 ppm) and deuterated CD_2Cl_2 (5.32 ppm). ^{31}P {H} chemical shifts are reported relative to an external, unlocked sample of H_3PO_4 (δ = 0.0 ppm). UV-Visible spectra were recorded on Cary 100 Conc. UV-Visible spectrophotometer and emission studies were carried out on HORIBA FluoroMax-4 spectrofluorometer. The diffraction data from single crystals of **4** and **5** mounted on a loop were collected at 100 K on an ADSC Quantum 210 CCD diffractometer with synchrotron radiation (λ = 0.90000 Å) at the Macromolecular Crystallography Beamline 6B1, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The raw data were processed and scaled using the program HKL2000. The structure was solved by direct methods, and the refinements were carried out with full-matrix least-squares on F^2 with appropriate software implemented in SHELXTL program package. The aromatic rings and PEt_3 groups of complex **4** with a dynamic motion were refined using SADI restraints. In addition, ISOR and SIMU restraints were adapted to restrain the anisotropic displacement parameters (ADPs) of H_2O and PEt_3, $OSO_2CF_3^-$ and diethyl ether, respectively. In the case of complex **5**, $OSO_2CF_3^-$, PEt_3, and CH_2Cl_2 were refined using the SADI, DFIX, DELU and SIMU restraints because of their dynamic motions. Moreover, the aromatic rings of complex **5** were adapted to their regular hexagonal geometries by FLAT restraint. All $OSO_2CF_3^-$ anions for complex **4** were observed in the difference Fourier map, while one independent counter anion for complex **5** was not observed in the density map because of the disorder problem.

Emission quenching titration

Solutions (5×10^{-6} M) of the squares were prepared in THF and aliquots (2 mL) were transferred to a 1-cm fluorescence cuvett. To this solution of square was added a stock solution (1×10^{-4} M) of the quencher in THF in an incremental manner. For all measurements emission wavelengths were monitored at $\lambda_{exc} = 342$ nm. Both the excitation and emission slit widths were 5 nm. Stern-Volmer quenching constant (K_{SV}) was estimated by fitting the intensity data acquired to the Stern-Volmer equation ($[I]_0/[I] = K_{SV}[\mathbf{Q}] + 1$).

Synthesis of 4. To a dichloromethane solution (0.5 mL) of Pd acceptor **1** (4.8 mg, 0.005 mmol) was added drop-by-drop a dichloromethane solution (0.5 mL) of **3** (3.2 mg, 0.005 mmol) with continuous stirring for three hours at room temperature. The wine red product **4** was isolated as a precipitate by adding ether to the dichloromethane solution. Yield: 95%. ^{1}H NMR (300 MHz, CD_3COCD_3): δ 8.51 (d, 16H, Py-H_α), 6.74 (d, 16H, Py-H_β), 7.60-7.95 (m, 80H, H-phenyl), 4.75-4.82 (t, 32H, Cp-H), 1.96 (m, 48H, PCH_2CH_3), 1.02 (m, 72H, PCH_2CH_3); ^{31}P {^{1}H} NMR (121 MHz, CD_3COCD_3): δ 32.9(s), δ 12.33 (s, $^1J_{PPt}$ = 1189Hz, P side). ESI-MS: *m/z* = 2094 [(M-$3CF_3SO_3)^{3+}$].

Synthesis of 5. To a dichloromethane solution (0.5 mL) of Pt acceptor **2** (5.2 mg, 0.005 mmol) was added a dichloromethane solution (0.5 mL) of **3** (3.2 mg, 0.005 mmol) drop-by-drop with continuous stirring for three hour at room temperature. The yellow product **5** was isolated as a precipitate by adding ether to the dichloromethane solution. Yield: 97%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.38(d, 16H, Py-H_α), 6.38 (d, 16H, Py-H_β), 7.53-7.81 (m, 80H, H-phenyl), 4.54-4.70 (t, 32H, Cp-H), 1.89 (m, 48H, PCH_2CH_3), 1.02 (m, 72H, PCH_2CH_3); ^{31}P {^{1}H} NMR (121 MHz,

CD_2Cl_2): δ 3.74(s, $^1J_{PPt}$ = 1681Hz, P-acceptor), δ 11.85 (s, $^1J_{PPt}$ = 1148Hz, P-donor). ESI-MS: *m/z* = 1976 [$(M- 3CF_3SO_3)^{3+}$].

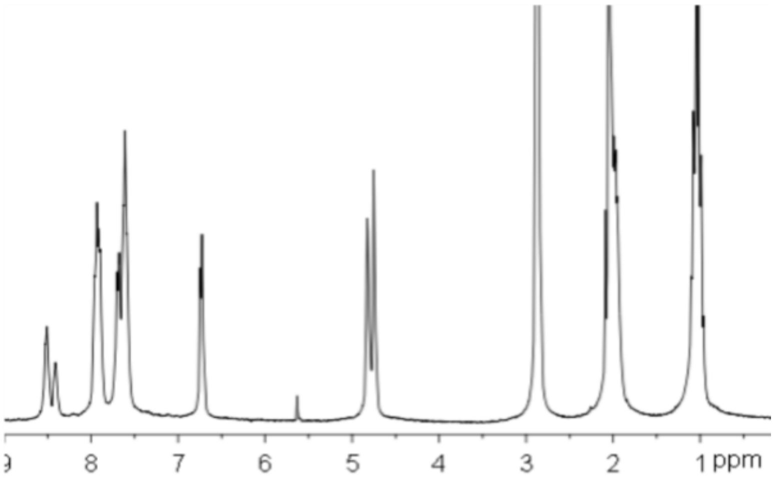

Figure S1. ^1H NMR Spectra of compound **4 (**CD_3COCD_3).

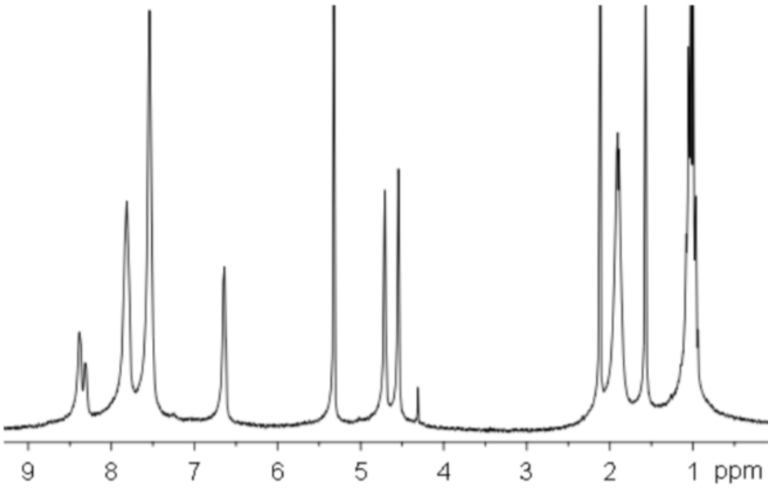

Figure S2.^1H NMR Spectra of compound **5 in** CD_2Cl_2.

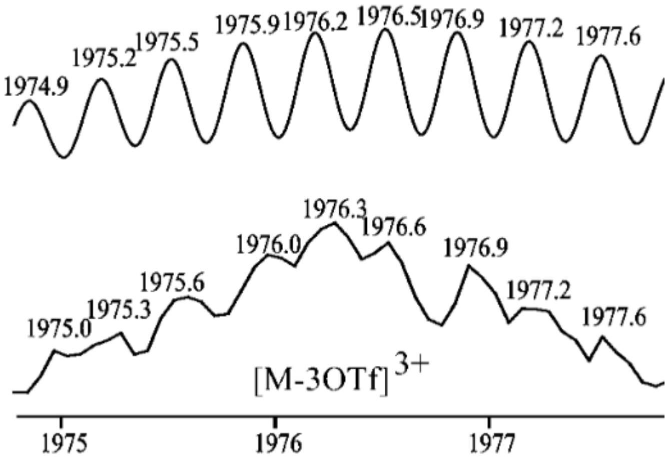

Figure S3. Calculated (top) and experimental (bottom) isotopic distribution patterns of the peak due to [M-3CF_3SO_3]$^{3+}$ fragment of **4** (M = molecular mass of **4**).

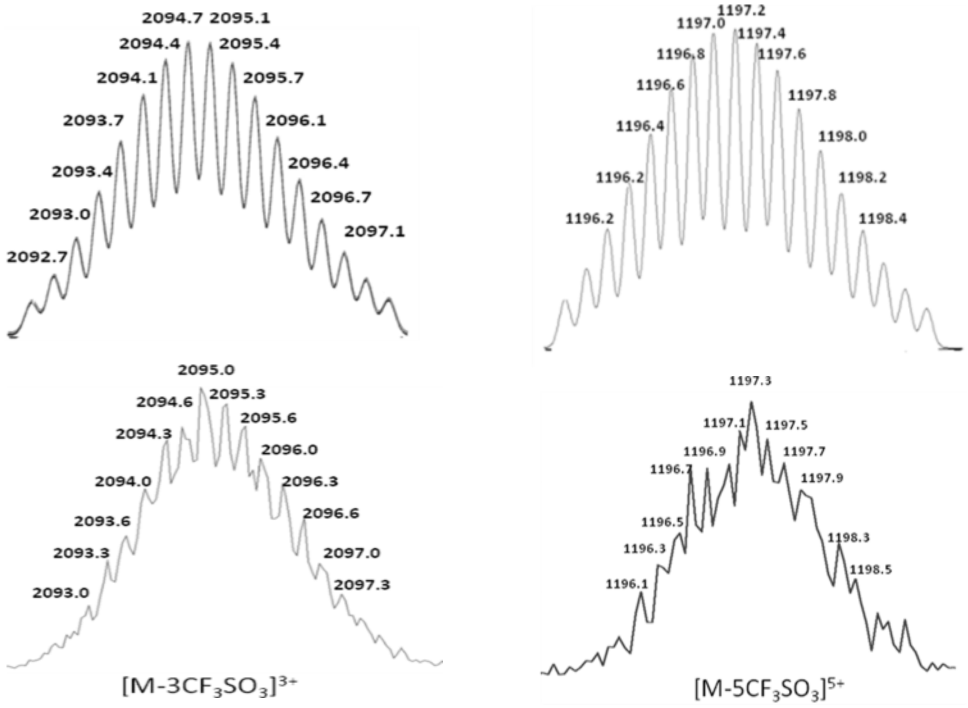

Figure S4. Calculated (top) and experimental (bottom) isotopic distribution patterns of the peaks due to [M-3CF_3SO_3]$^{3+}$ (left) and [M-5CF_3SO_3]$^{5+}$ (right) fragments of **5** (M = molecular mass of **5**)

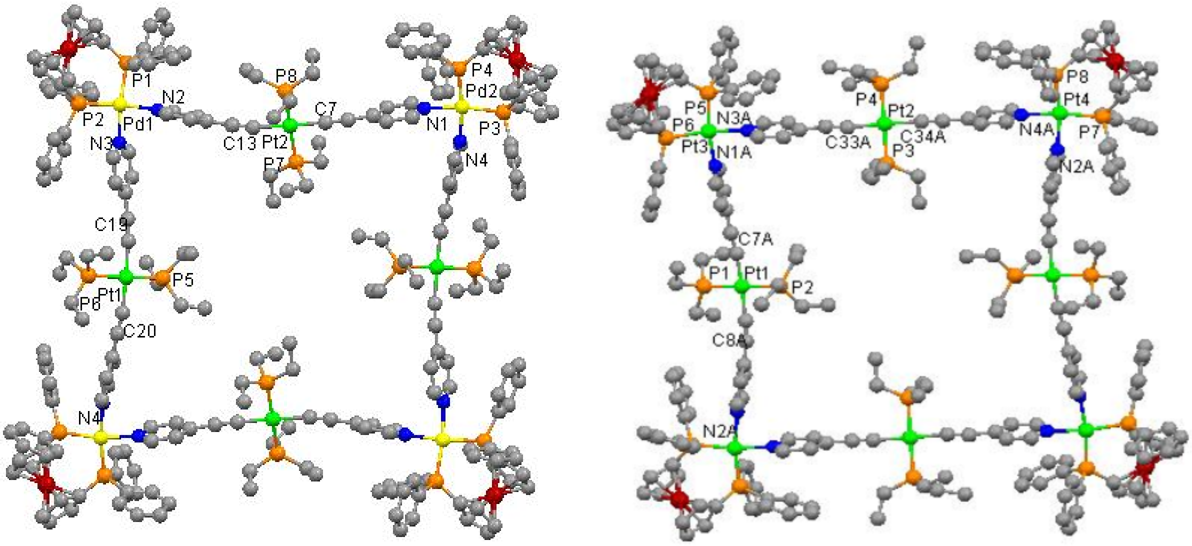

Figure S5. Numbered crystal diagram for complex **4** (left) and **5** (right). Color codes: yellow = Pd, green = Pt, brown = Fe, brownish yellow = P, gray = C.

Table 1. Important Bond Lengths (Å) and Angles (º) for the Complexes **4** and **5**.

Complex **4**

Pt(1)-C(20) 1.986(15) Pd(1)-P(1) 2.309(3)

Pt(1)-C(19) 1.976(14) Pd(1)-N(3) 2.078(10)

Pt(1)-P(5) 2.299(4) Pd(1)-N(2) 2.090(10)

Pt(1)-P(6) 2.309(4) Pd(1)-P(2) 2.309(3)

Pt(2)-C(7) 1.947(14) Pd(2)-N(4) 2.088(11)

Pt(2)-C(13) 2.012(16) Pd(2)-N(1) 2.082(10)

Pt(2)-P(7) 2.299(5) Pd(2)-P(4) 2.291(3)

Pt(2)-P(8) 2.296(5) Pd(2)- P(3) 2.288(3)

C(20)- Pt(1)-C(19) 176.5(6) N(1)-Pd(2)-N(4) 83.8(4)

C(19)- Pt(1)-P(5) 91.6(4) N(1)-Pd(2)-P(3) 170.2(3)

C(20)- Pt(1)-P(6) 91.6(5) P(3)-Pd(2)-P(4) 100.97(13)

C(19)- Pt(1)-P(6) 87.6(4) N(3)-Pd(1)-N(2) 83.4(4)

P(5)- Pt(1)-P(6) 177.46(16) N(2)-Pd(1)-P(2) 173.1(3)

C(7)-Pt(2)-C(13) 177.3(6) P(1)-Pd(1)-P(2) 98.73(11)

C(7)-Pt(2)-P(7) 87.8(5)

Complex **5**

Pt(1)-C(7A) 2.04(3) Pt(3)-P(5) 2.286(5)

Pt(1)-P(2) 2.282(5) Pt(3)-P(6) 2.290(4)

Pt(3)-N(3A) 2.125(14) Pt(4)-N(2A) 2.130(16)

Pt(3)-N(1A) 2.132(17) Pt(4)-P(7) 2.289(4)

C(7A)-Pt(1)-C(8A) 177.7(9) N(3A)-Pt(3)-P(5) 87.3(4)

C(7A)-Pt(1)-P(2) 89.5(5) P(5)-Pt(3)-P(6) 99.13(17)

P(2)-Pt(1)-P(1) 178.5(2) P(8)-Pt(4)-P(7) 101.71(18)

N(3A)-Pt(3)-N(1A) 82.3(6) N(2A)-Pt(4)-P(7) 88.3(3)

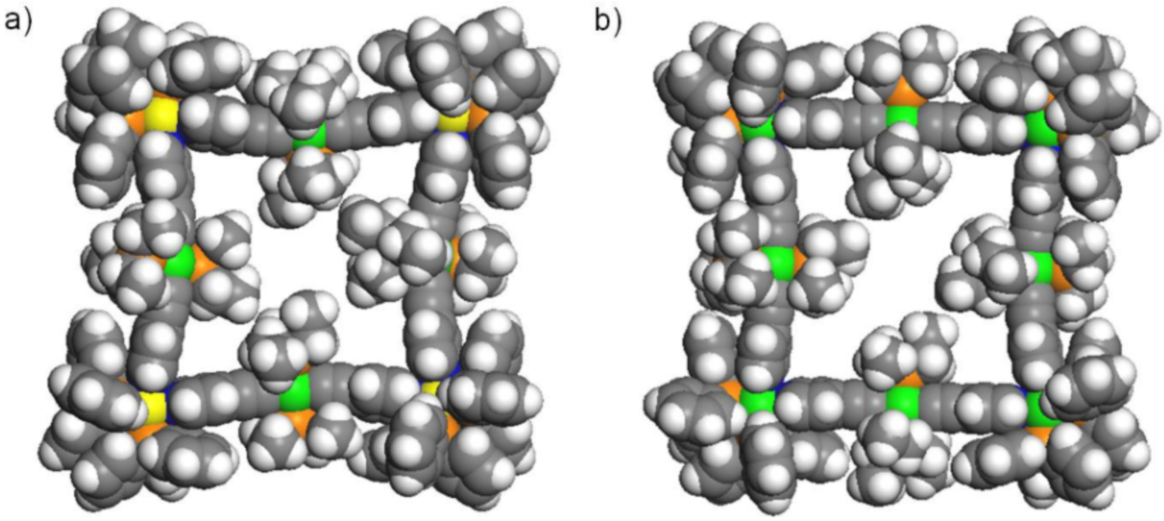

Figure S6. CPK drawing of X-ray structure **4** (left) and **5** (right)

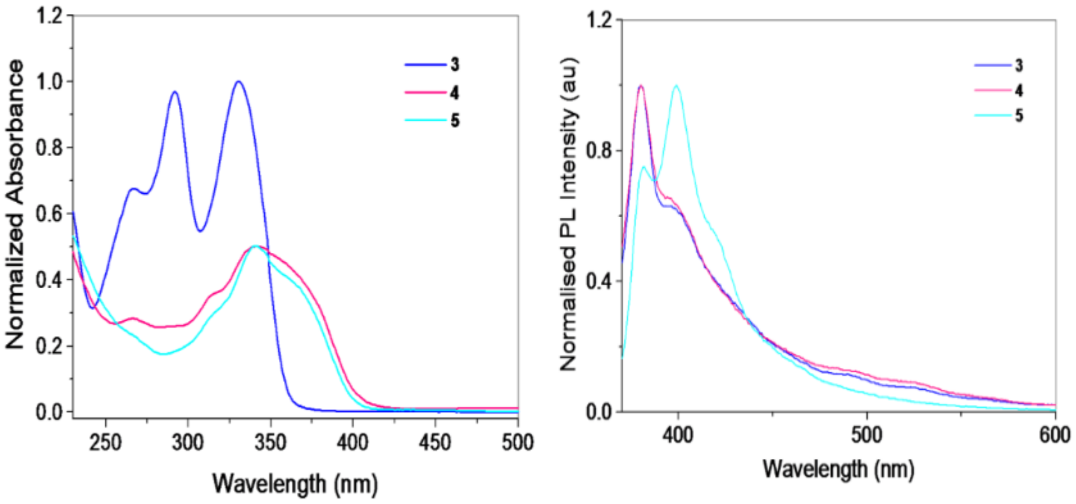

Figure S7. UV-vis (left) and emission (right) spectra of **3-5** in THF.

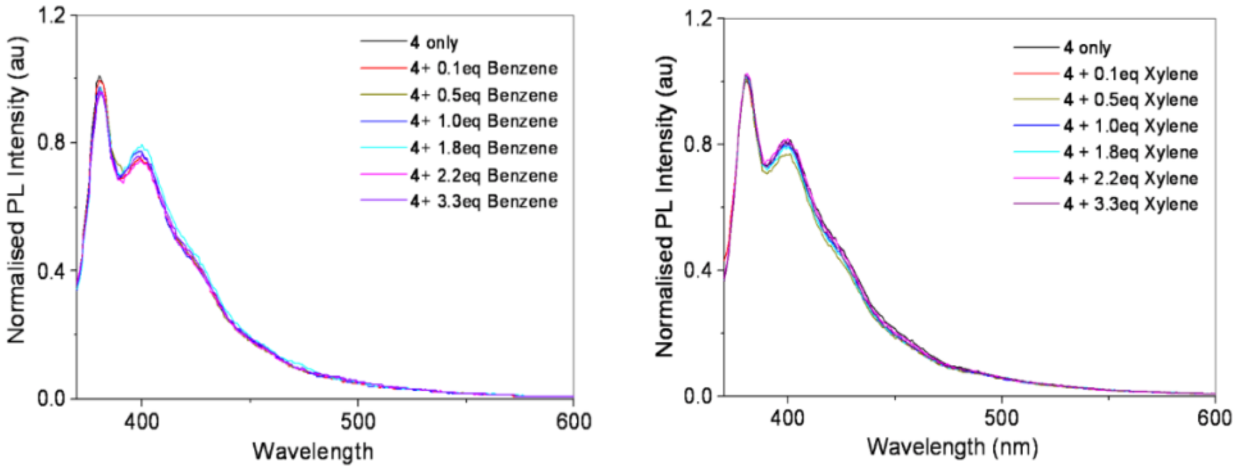

Figure S8. Changes in the emission spectra of complex **4** upon addition of increasing amounts of Benzene (left) and Xylene (right) analyte.

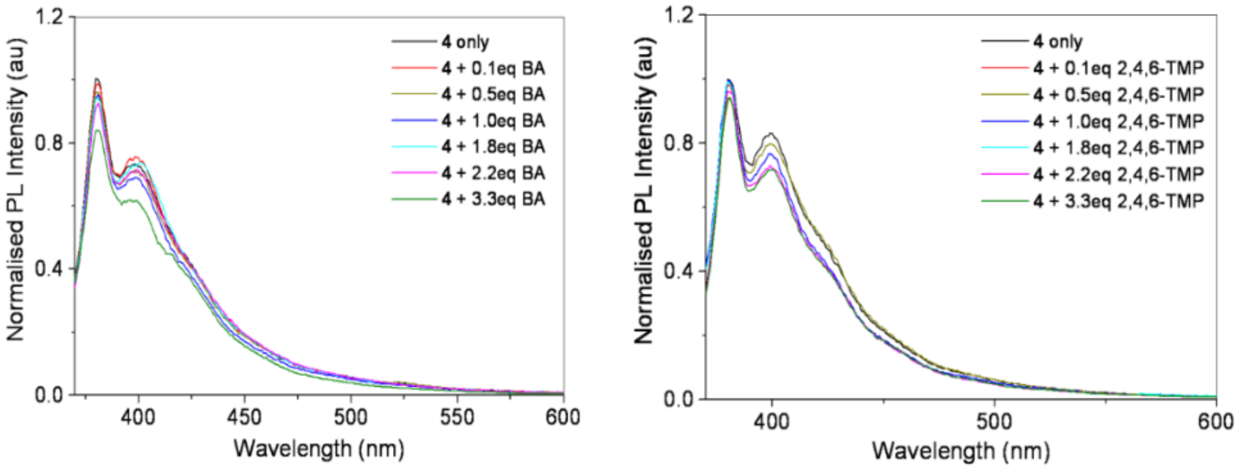

Figure S9. Changes in the emission spectra of complex **4** upon addition of increasing amounts of BA (left) and 2,4,6-TMP (right) analyte.

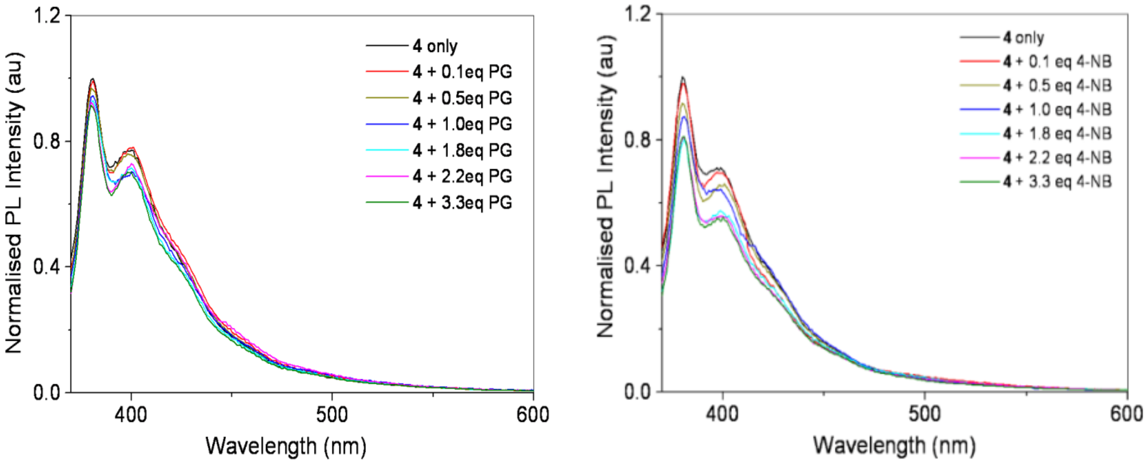

Figure S10. Changes in the emission spectra of complex **4** upon addition of increasing amounts of PG (left) and 4-NB (right) analyte.

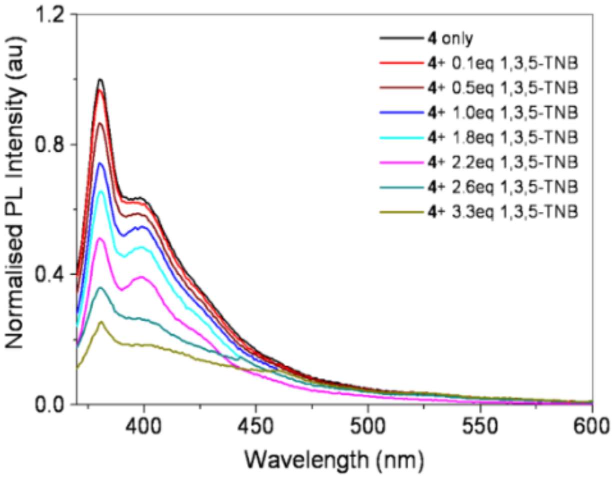

Figure S11. Changes in the emission spectra of complex **4** upon addition of increasing amounts of 1,3,5-TNB analyte.

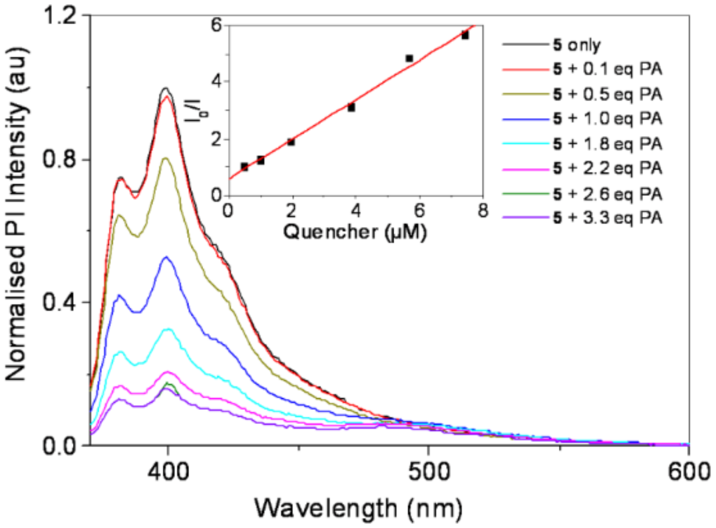

Figure S12. Changes in the emission spectra of complex **5** upon addition of increasing amounts of Picric Acid analyte and Stern-Volmer Plot (inset).

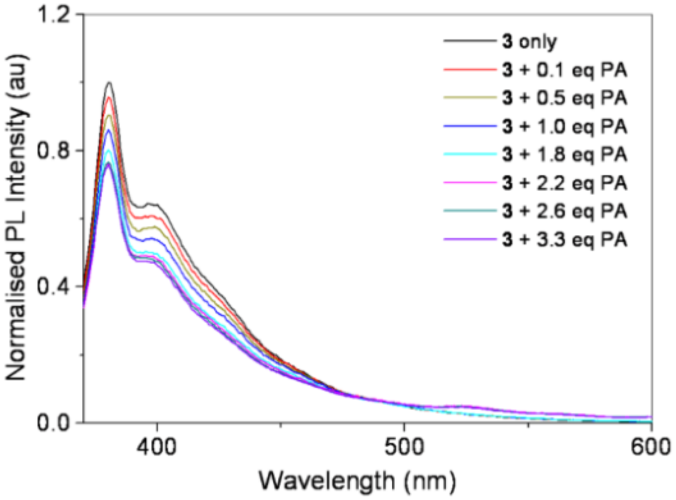

Figure S13. Changes in the emission spectra of donor **3** upon addition of increasing amounts of Picric Acid analyte.

References:

1. D.-Y. Noh, E.-M. Seo, H.-J. Lee, H.-Y. Jang, M.-G. Choi, Y. H. Kim, J. Hong, *Polyhedron*, 2001, **20**, 1939.
2. Y. K. Kryschenko, S.R. Seidel, A.M. Arif, P.J. Stang, *J. Am. Chem. Soc.,* 2003, **125**, 5193.