Supporting Information for

Unusual face-to-face π–π stacking interactions within an indigo-pillared M_3(tpt)-based triangular metalloprism

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Spectral characterization details for 3

Fluorescence quenching studies

The electronic absorption spectra were recorded on a Hewlett Packard 8453 spectrophotometer. Steady-state emission spectra were obtained in THF solution at ambient temperature with a Hitachi F-4500 fluorescence spectrophotometer. Quenching experiments of the fluorescence of **3** were carried out under aerated conditions. The excitation wavelength was 335 nm in THF as the solvent. The monitoring wavelength corresponded to the maximum of the emission band at 392 nm. Relative fluorescence intensities were measured for solutions of **3** in THF and nitroaromatics used as quenchers. There was no change in shape, but a change in the intensity of the fluorescence peak was found, when the nitroaromatics were added. The Stern-Volmer (SV) relationship, $I_o/I = 1 + K_{sv}[Q]$, was obtained for the ratio of the emission intensities (I_o and I are the emission intensities in the absence and presence of quencher) and quencher concentration, [Q]. The quenching rate constants were obtained from the Stern-Volmer constant, K_{sv}, and the fluorescence lifetime, τ, of **3** (5.5 ns). Excited-state lifetime studies were performed using an Edinburgh FL 920 single photon-counting system with a hydrogen-filled lamp or a nitrogen lamp as the excitation source. The emission decays were analyzed by the sum of exponential functions, which allows the partial elimination of instrument time broadening, thus rendering a temporal resolution.

Binding constant measurements

The binding abilities of **3** with nitroaromatics was examined by emission spectroscopic method. The concentration of **3** was 3×10^{-5} M and the nitroaromatics were $2 \times 10^{-4} - 8 \times 10^{-3}$ M. The binding constants from the electronic absorption experiment were measured by changing the concentration of nitroaromatics with **3** at 355 nm and calculated on the basis of the Benesi-Hildebrand relationship for 1:1 molar ratio. The quadratic relationship between I_o/I and [Q] predicted an upward curvature in the Stern-Volmer plot. In order to explain the non-linearity of the curve, the following extended Stern-Volmer equation was used.

$$I_o/I = (1 + K_D[\text{host}])\ (1 + K_S[\text{host}])$$

where K_D and K_S are the dynamic and static Stern-Volmer constants respectively. A non-linear plot of above eqn suggests the presence of a static component in quenching mechanism along with dynamic quenching. The close resemblance of the experimental data to the theoretical fits using an emission method is supportive of a 1:1 complexation. Further, the high value of the quenching rate constant, $k_{q,}$ indicates efficient bimolecular quenching between **3** and nitroaromatics, along with binding.

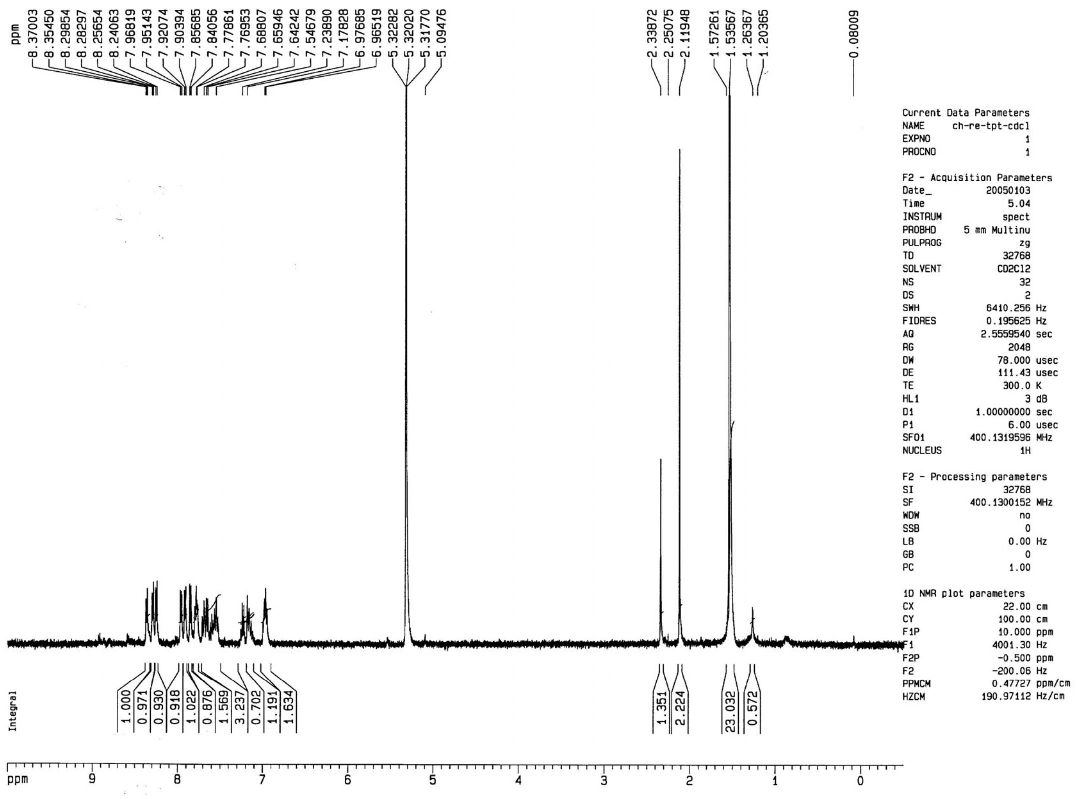

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Fig. S1 ^{1}H NMR spectrum of **3** in CD_2Cl_2.

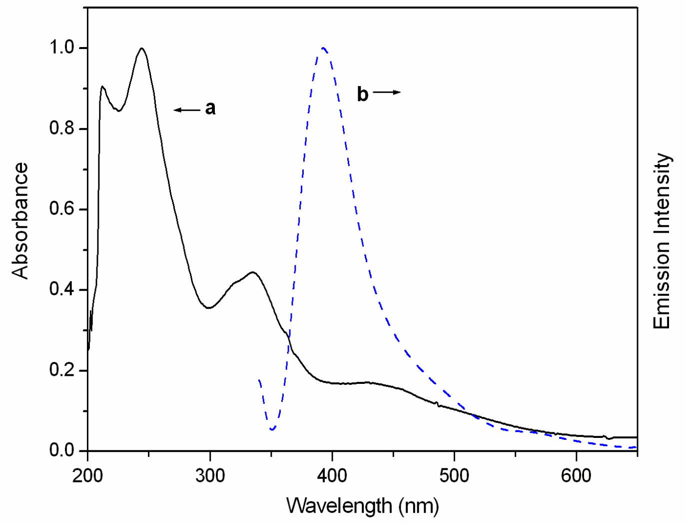

Fig. S2 (a) Absorption and (b) emission spectrum of **3** in THF at room temperature.

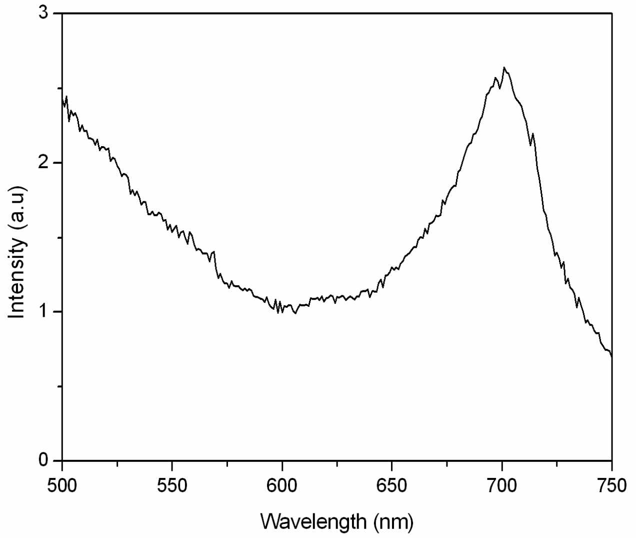

Fig. S3 Emission spectrum of **3** at 77 K in THF.

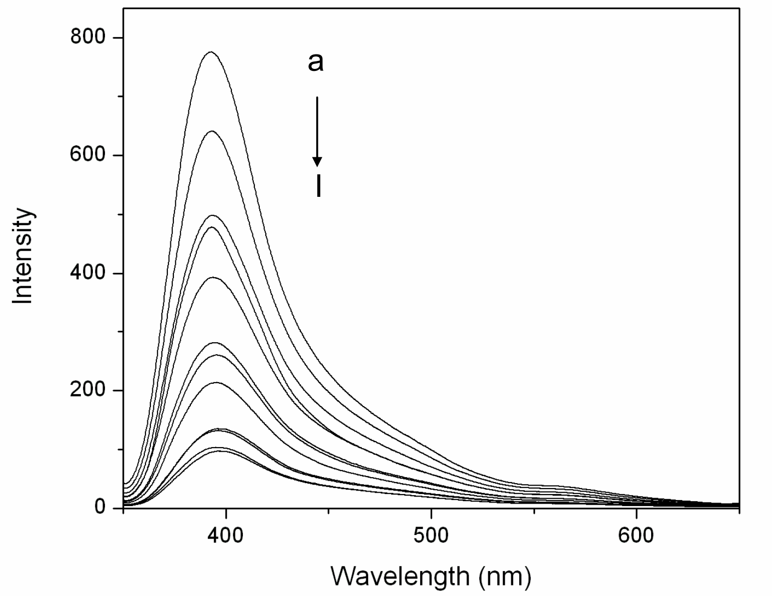

Fig. S4 Emission intensities of **3** decreasing with the quencher (*p*-nitrotoluene) concentration in the range of (a) 0 M, (b) 4 × 10^{-4} M, (c) 8 × 10^{-4} M, (d) 12 × 10^{-4} M, (e) 16 × 10^{-4} M (f) 20 × 10^{-4} M (g) 24 × 10^{-4} M (h) 28 × 10^{-4} M (i) 32 × 10^{-4} M (j) 36 × 10^{-4} M (k) 40 × 10^{-4} M and (l) 44 × 10^{-4} M in THF.

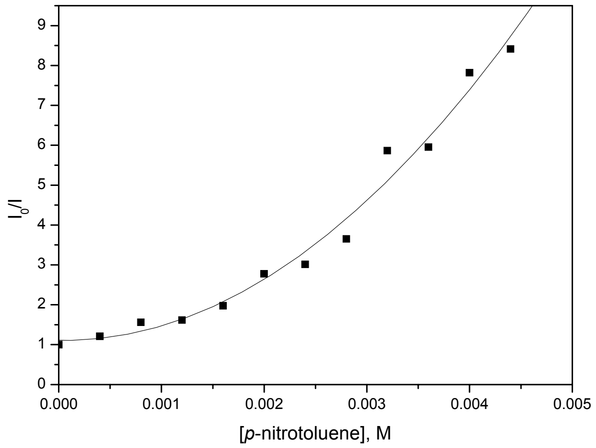

Fig. S5 Stern-Volmer plot for the emission quenching of **3** with the different concentration of *p*-nitrotoluene in THF.

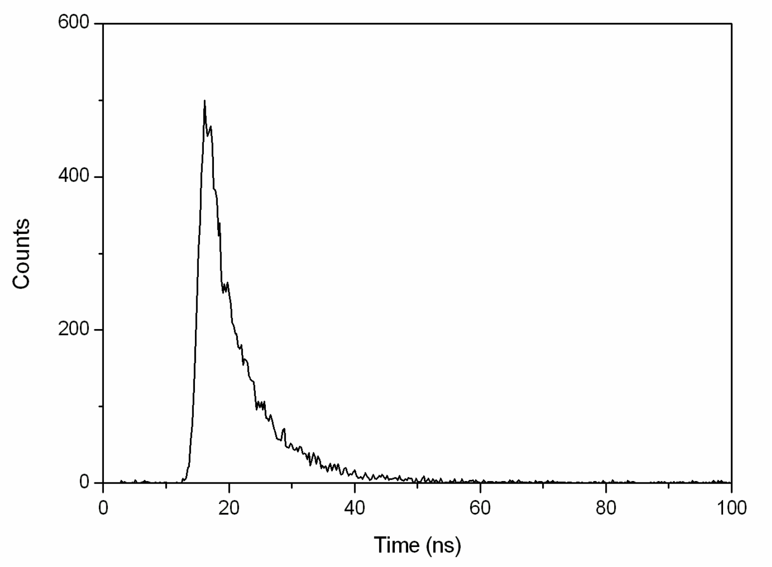

Fig. S6 Decay profile recorded for the emission from **3** in THF at 298 K upon excitation at 335 nm.

Table S1 Affinity constants of **3** with nitroaromatic guests in THF at 25 °C.

Guests	K_a, M^{-1}
nitrobenzene	3.3×10^2
1,4-dinitrobenzene	2.7×10^2
1,2-dinitrobenzene	1.4×10^3
p-nitrotoluene	4.2×10^3
1-chloro-4-nitrobenzene	2.0×10^2