Supporting Information

1. The definition of r[S1]

$$r = \frac{C_{TPPY}}{C_{AuNPs}}$$

C_{TPPY}: concentration of TPPY; **C_{AuNPs}: concentration of Au NPs**

The concentration of the Au NPs is calculated as follows:

(1) The weight of Au (W_{Au}) produced from the complete reduction of $HAuCl_4$ is calculated by multiplying the mole of added $HAuCl_4$ (weight of added $HAuCl_4$·4H2O divided by molecular weight (MW) of $HAuCl_4$·$4H_2O$) with the atomic weight of Au (196.97 g/mol).

(2) The volume of generated Au (V_{Au}) is calculated by dividing the weight of produced Au (W_{Au}) by the density of Au (d) (19.32 g/cm^3).

$$V_{Au} = \frac{W_{Au}}{d_{Au}}$$

(3) The number of Au NPs (diameter (D) 5nm) is computed by dividing the volume of generated Au (V_{Au}) by the volume of an individual Au NPs ($\pi D^3/6$). The mole of Au nanoparticles is then determined by dividing the number of Au nanoparticles by Avogadro's constant (6.02×10^{23}).

(4) The molar concentration of Au nanoparticles is calculated by dividing the mole of Au nanoparticles by the solution volume.

$$C_{AuNPs} = \frac{n_{AuNPs}}{V_{sol}}$$

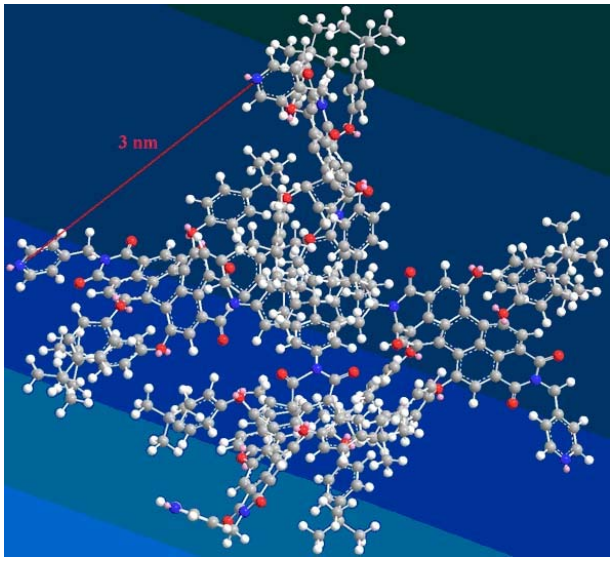
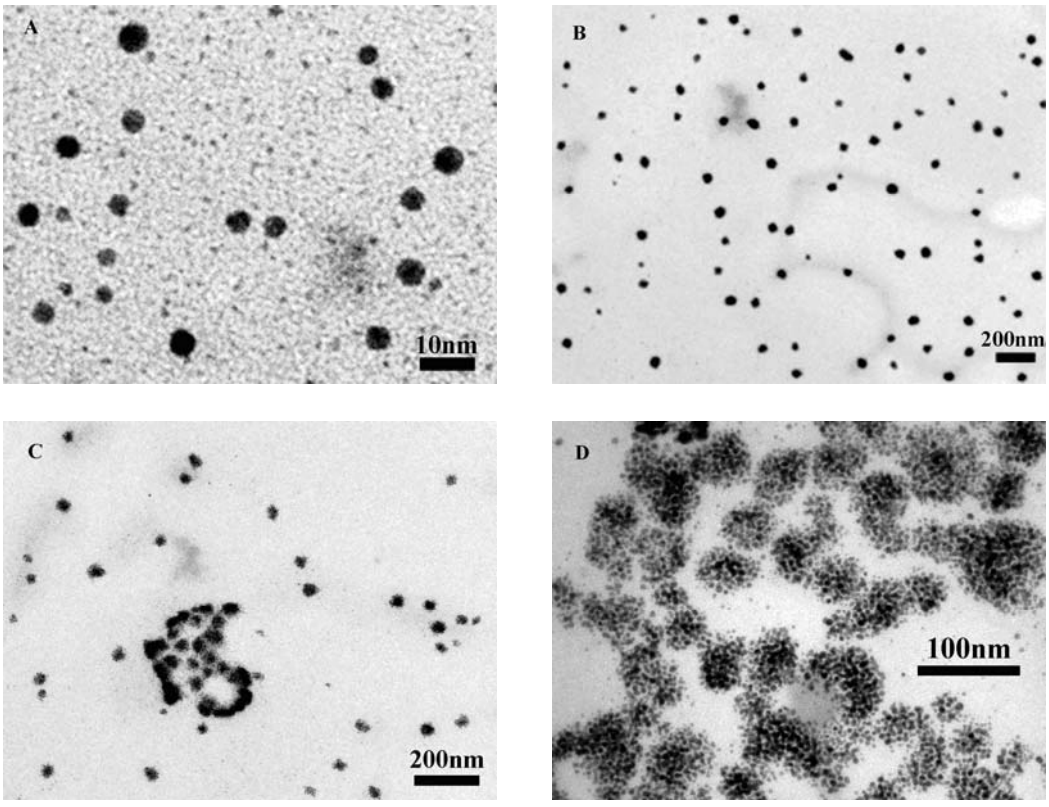


Figure S1. The minimum energy simulation of ligand **TPPY** with the MM2 minimum energy method.



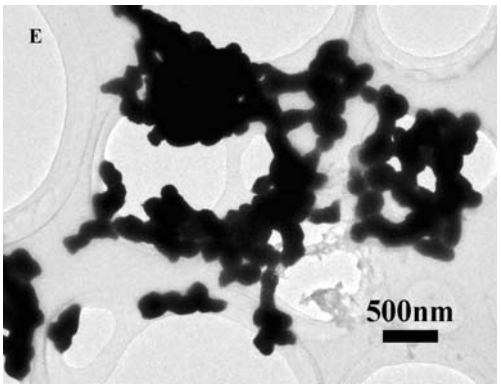


Figure S2. TEM images: (A) near 5nm mono-disperse Au NPs; (B) [**TPPY**] = 5×10^{-5} M; (C) [**TPPY**] = 1×10^{-4} M; (D) magnification of some areas of Figure **7C**; (E) [**TPPY**] = 5×10^{-4} M; (F) [**TPPY**] = 1×10^{-3} M.

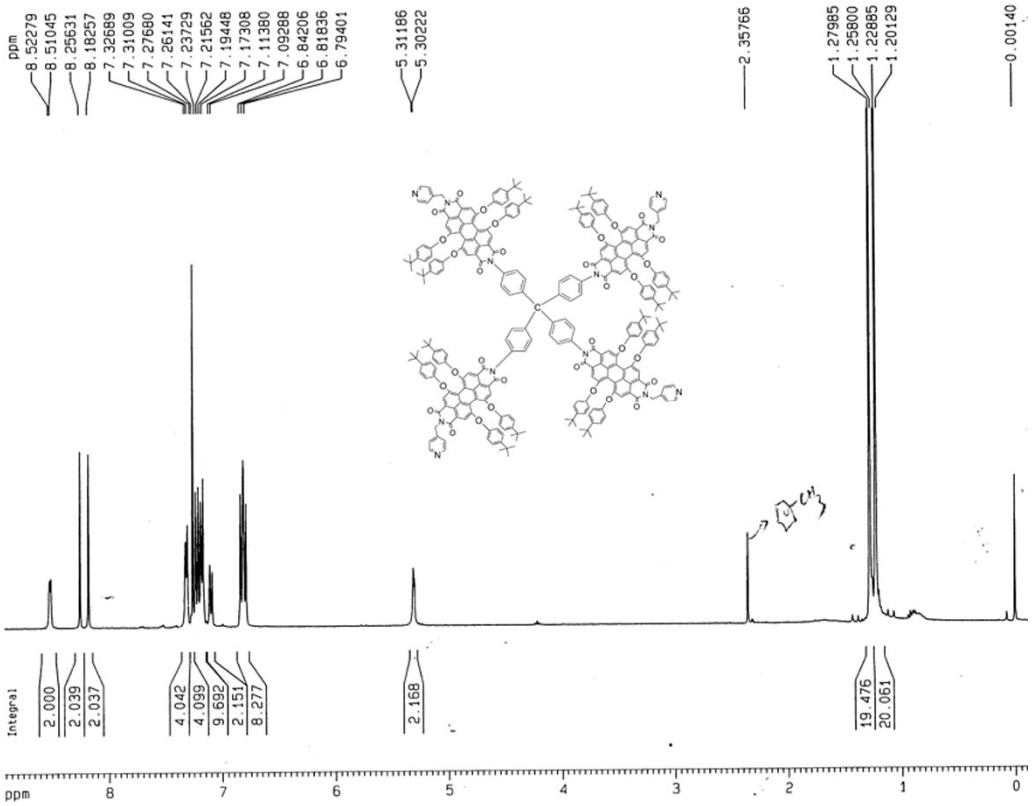


Figure S3 H^1 NMR of **TPPY**

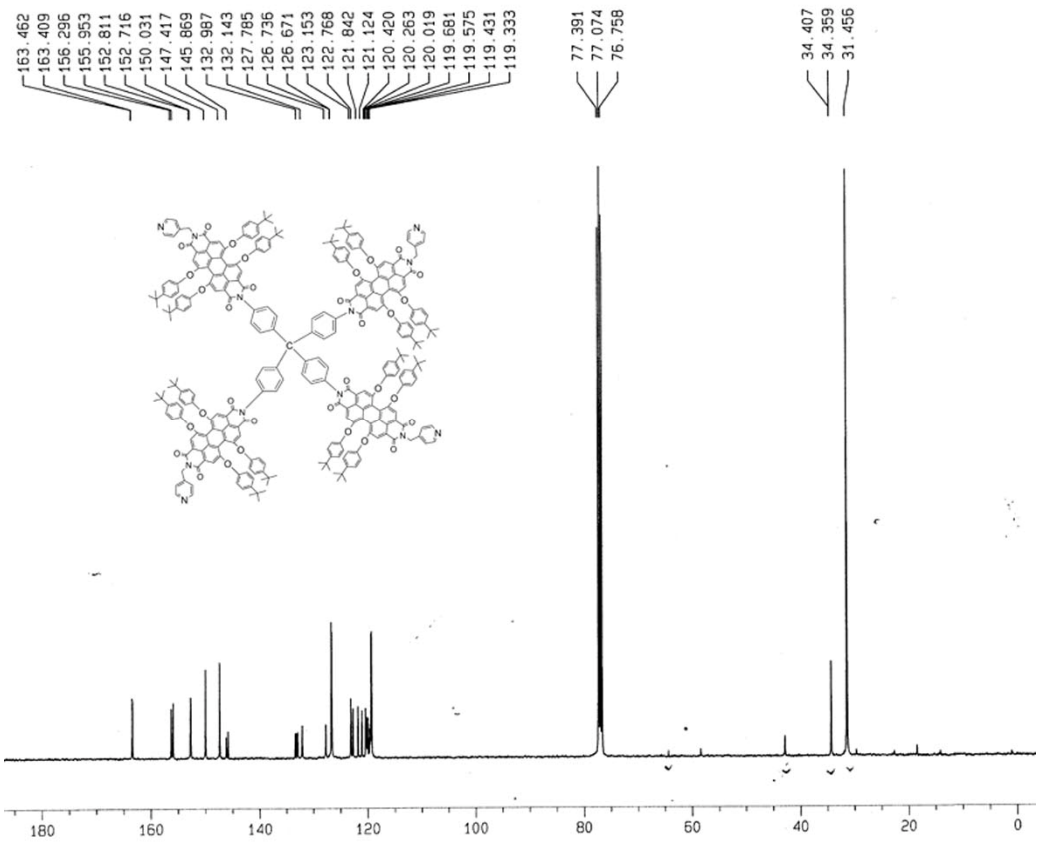


Figure S4 C^{13} NMR of **TPPY**

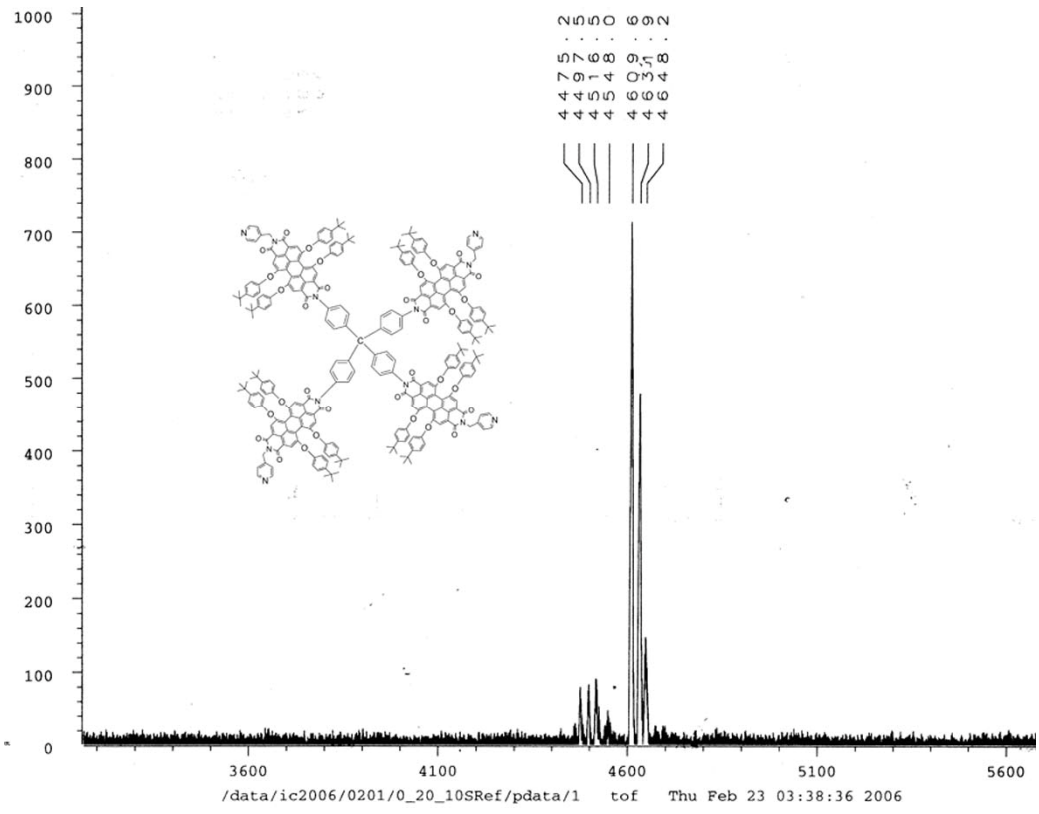


Figure S5 MALDI-TOF of **TPPY**

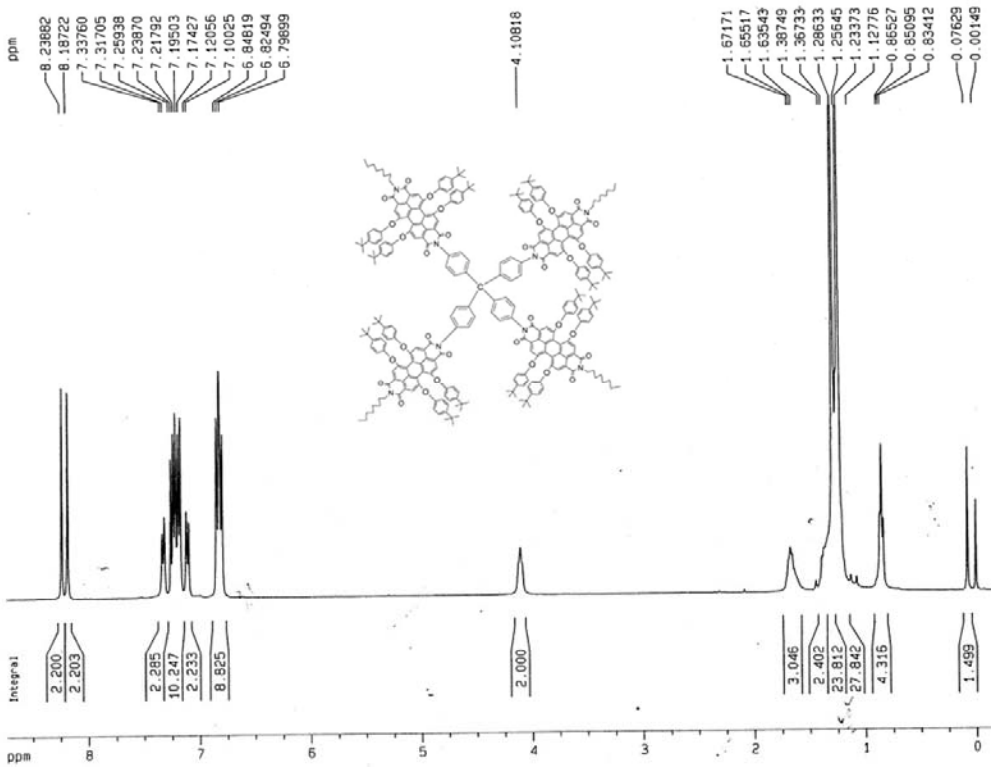


Figure S6 H^1 NMR of **TPOT**

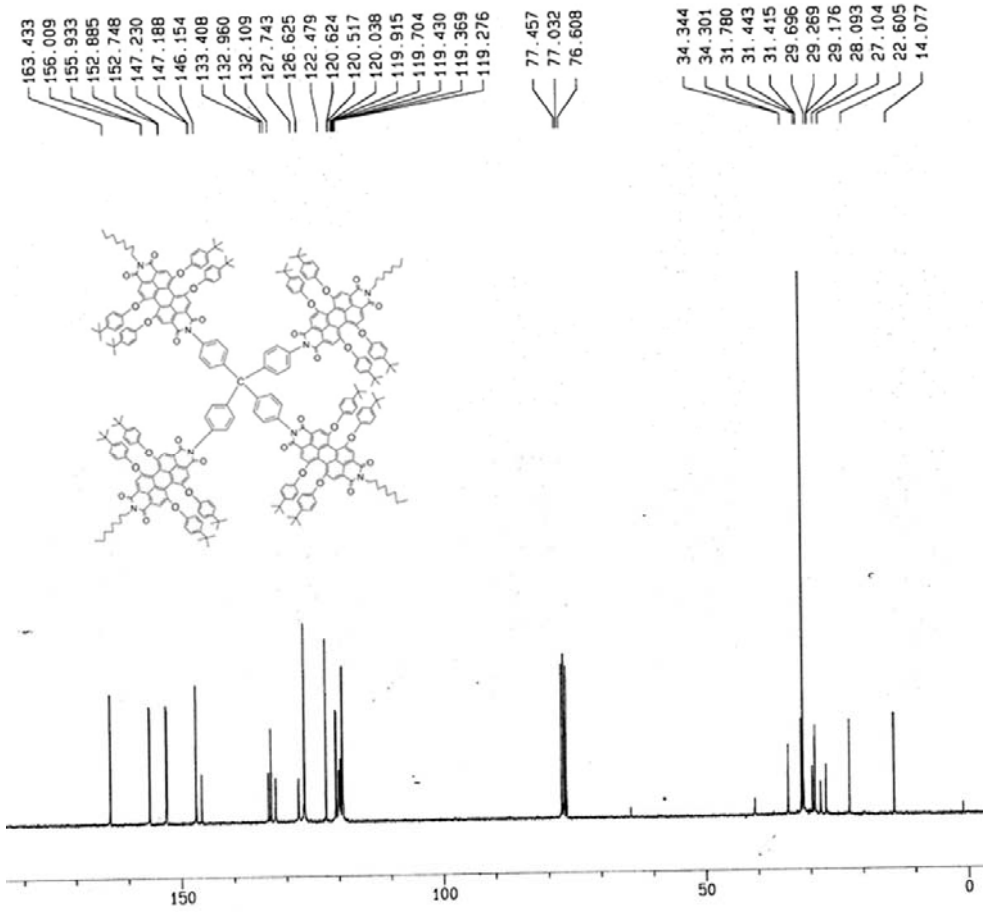


Figure S7 C^{13} NMR of **TPOT**

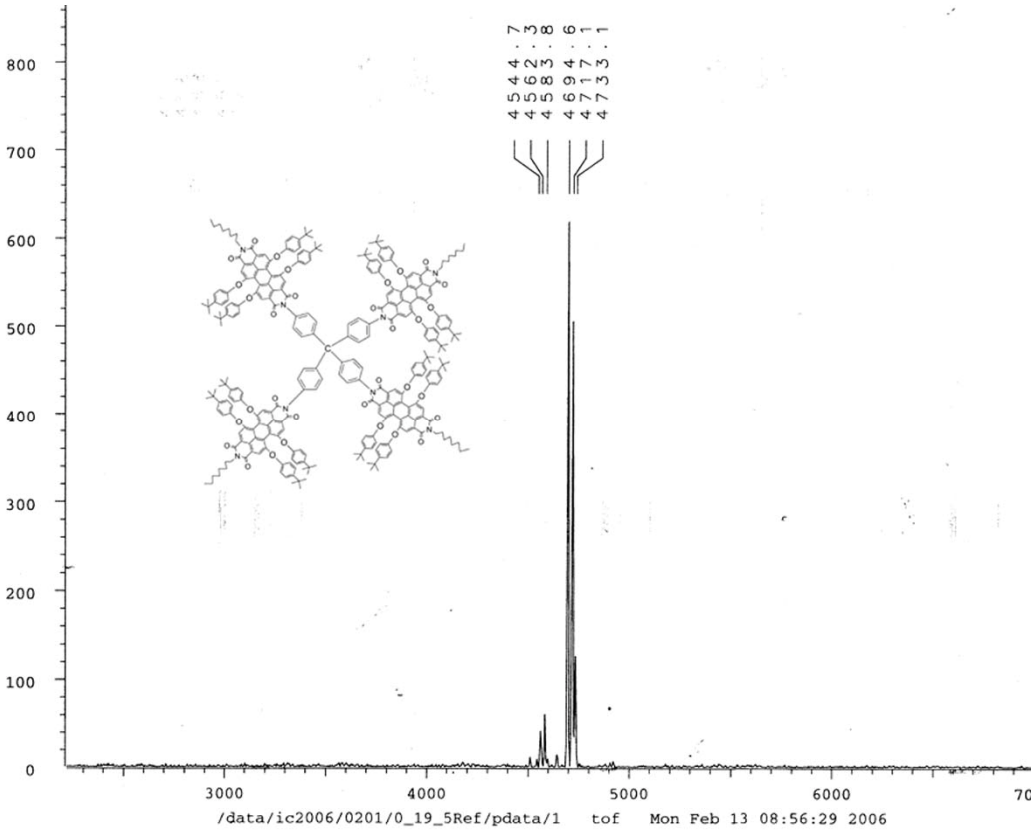


Figure S8 MALDI-TOF of **TPOT**

[S1]. Xu, X-H; Huang, S.; Brownlow, W.; Salaita, K.; Jeffers, R. B. *J. Phys. Chem. B* **2004**, 108, 15543-15551.