

# **Perylenebisimide-based Multi-modal Cyanide Recognition: Molecular Logic Gate Deciphering Magnetic Memory Units**

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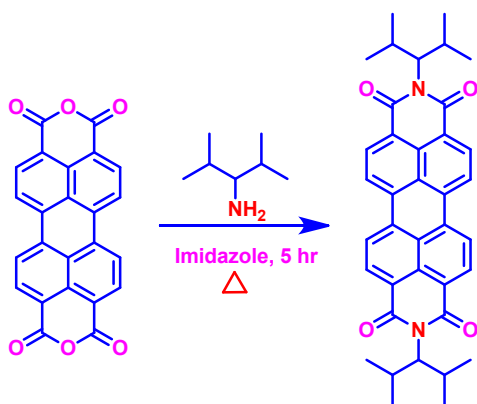
## General Methods

**1.1 Materials and reagents:** Spectroscopic grade solvents were used for measuring electrochemical and optical properties. Unless otherwise noted, the chemicals received from Sigma Aldrich were used without further purification. All the reactions as well as electrochemical measurements were carried out under either argon atmosphere. Solvents were dried according to routine procedures. Samples synthesized were purified by column chromatography using silica gel (230-400 mesh) from Merck followed by recrystallization.

**1.2 Steady-state absorption and emission measurements:** Steady-state absorption spectra were obtained by using UV/VIS/NIR spectrometers (Varian, Cary5000). Silica cell with optical path length of 10 mm was used for all steady-state measurements. Tetrahydrofuran was obtained from Sigma-Aldrich (spectroscopic grade). Steady-state fluorescence emission measurements were done on a Horiba Jobin Yvon fluorolog 3-111. Quartz cell with optical path length of 10 mm was used for all fluorescence measurements.

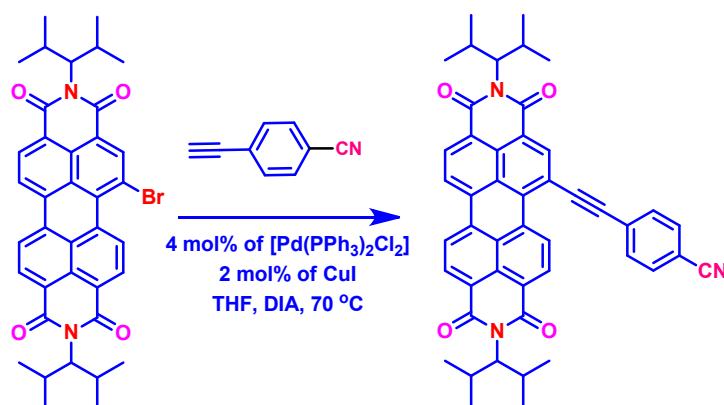
**1.5 EPR- Spectra** were recorded on a Bruker Elexsys X-band spectrometer at room temperature.

### Synthesis:



**Scheme 1** Synthesis of *N,N'*-Bis(2,4-dimethylpent-3-yl)perylene-3,4:9,10-tetracarboxylic bisimides **1**

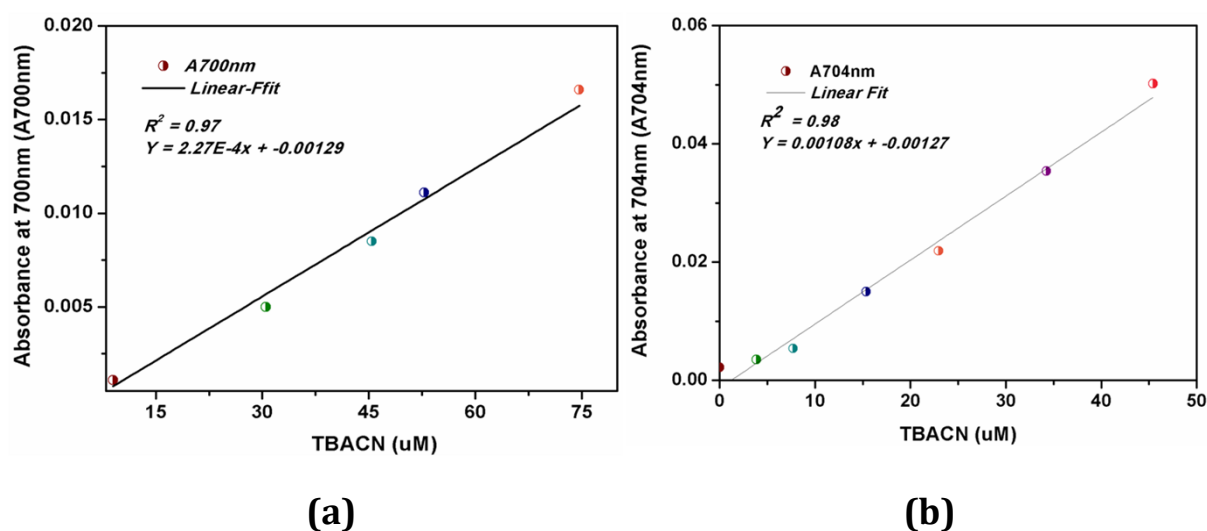
**Compound 1:** A mixture of 2,4-dimethylpent-3-ylamine (0.688 g, 2.35 eq), PDA (1 g, 1 eq) and imidazole (10.2 g, 60 eq) was stirred at 140°C for 5 h and diluted with ethanol. This was followed by the addition of 2M HCl (100mL). The reaction mixture was then allowed to settle down. The precipitates thus formed were collected through vacuum filtration and dried in oven. Further purification by silica gel chromatography using chloroform as eluent yielded the desired perylenebisimide **1** (1.17g, 80%). <sup>1</sup>H NMR (500MHz) (CDCl<sub>3</sub>) δ (ppm): 8.69 (m, 8H), 4.78 (t, J=7 Hz, 2H), 2.74 (m, 4H), 1.14 (d, J=7 Hz, 12H), 0.96 (d, J=7 Hz, 12H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): 165.22, 164.10, 139.32, 134.60, 134.54, 131.33, 129.61, 126.48, 123.19, 123.11, 123.07, 114.09, 65.19, 29.72, 29.15, 21.85, 20.63. HRMS: [M+H] 587.2904 (Calc.); 587.2903 (found).



**Scheme 2** Synthesis of **2**

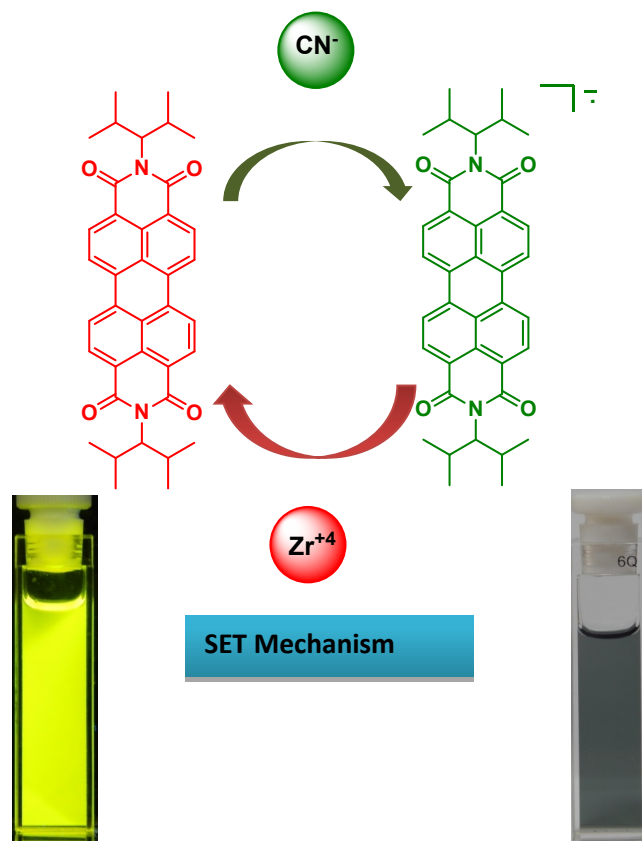
Compound **2** : A dry Schlenk tube was charged with  $[\text{PdCl}_2(\text{PPh}_3)_2]$  (1.3 mg, 4 mol%), CuI (0.6 mg, 2 mol%), dry THF (3 ml) and *N,N*-diisopropylamine (2 ml). The resulting solution was degassed vigorously under argon. This was followed by the addition of 1-Bromo -*N,N'*-Bis(2,4-dimethylpent-3-yl)perylene-3,4:9,10-tetra-carboxylicbisimide<sup>10a</sup> (30 mg, 1 eq) and 4-Ethynyl-benzonitrile (6.8 mg, 1.2 eq). The reaction mixture was refluxed at 70-80 °C. The progress of the reaction was monitored by TLC at regular intervals. After the completion of reaction, the solvent was evaporated under vacuum. The reaction mixture was mounted on a column with silica gel (230-400 mesh size) and was eluted with hex:chl (20:80). Further purification was done by recrystallization in hexane/ $\text{CH}_2\text{Cl}_2$  to get a red solid **2** in excellent yield (30.4 mg, 95%).  $^1\text{H}$  NMR (500MHz) ( $\text{CDCl}_3$ )  $\delta$  (ppm): 10.16 (d,  $J=8.26\text{Hz}$ , 2H), 8.92 (s, 1H), 8.90 (s, 1H) 8.76 (m, 10H), 7.80 (m, 8H), 4.79 (m, 4H), 2.75 (m, 8H), 1.15 (2d (merged),  $J=6.68$  Hz, 23H), 0.96 (d,  $J=6.76$  Hz, 23H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 165.21, 165.07, 165.01, 164.09, 163.97, 163.89, 163.43, 138.65, 138.04, 135.12, 131.5, 127.14, 131.50, 127.14, 123.72, 122.35, 118.21, 112.92, 96.42, 96.37, 94.68, 94.66, 65.41, 65.37, 65.29, 29.14, 29.13, 29.09, 29.06, 21.81, 21.76, 20.59, 20.55, 20.53. HRMS:  $[\text{M}+\text{H}]$  712.3170 (Calc.); 712.3182 (found).

## 5. Calibration Details

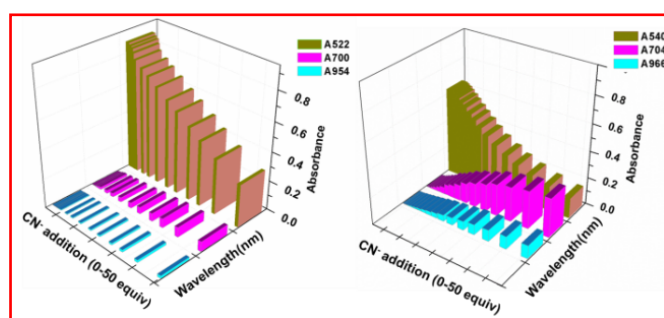


**Fig. S1.** Figure demonstrates the variations of absorption signal at 700nm in receptor **1**(a) and at 704nm in receptor **2** (b) with various concentrations of TBACN. Here concentration of receptor **1** and **2** used was  $17\mu\text{M}$  and  $5\mu\text{M}$  respectively.

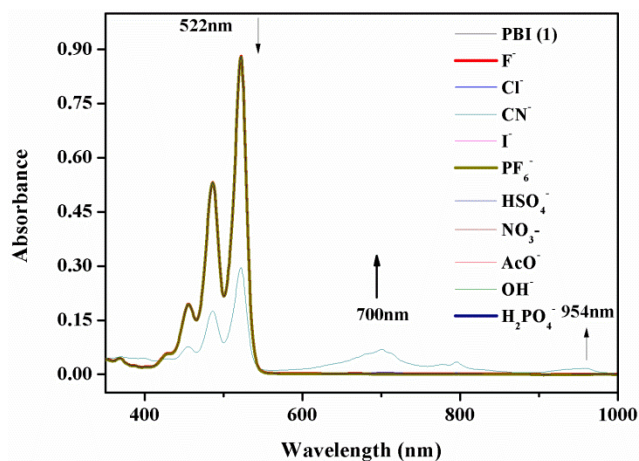
Calibration curves reflect the sensitivity of **2** and potential of receptor for calibrating cyanide up to 1  $\mu\text{M}$ . The wave length has been chosen due to its strong variations with trace amount of cyanide in visible region.



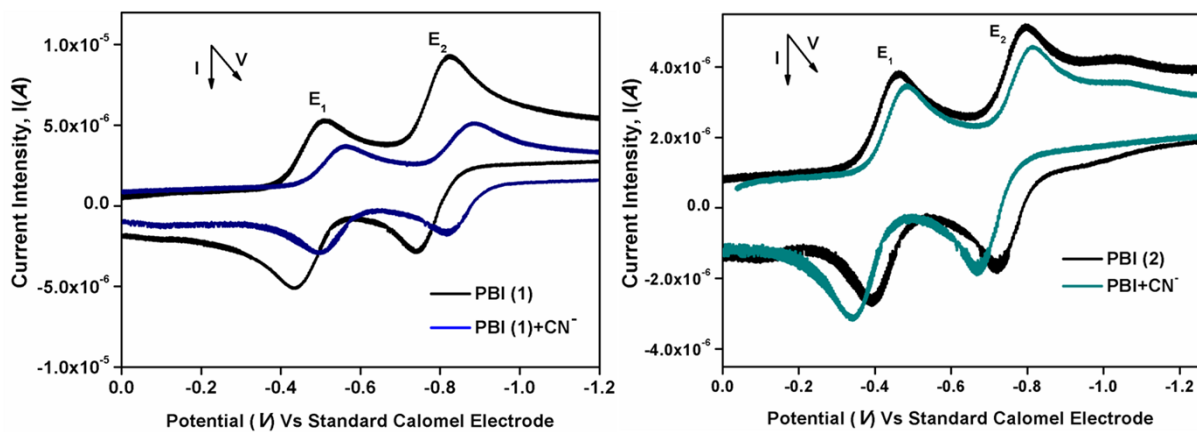
**Fig. S2.** Interaction of  $\text{CN}^-$  with **1** in THF: formation of PBI anion radical and reversal of SET with visible colorimetric and fluorescence changes in presence of cyanide.



**Fig. S3** 3D graphical representation of the sensitivity of **2** (right) in comparison of **1** (left) while probing changes in presence and absence of cyanide in visible and NIR region. The observations were made in presence of 50 equivalents of TBACN to PBI (**1** and **2**) with 6  $\mu\text{M}$  and 4.9  $\mu\text{M}$  respectively.



**Fig S4.** Absorption profile depicting selectivity for Cyanide anion by PBI (**1**, 18.5 $\mu$ M) under THF/H<sub>2</sub>O (v/v: 9/1) conditions at room temperature.



**FigS5.** Electrochemical (CV) changes in reduction waves ( $E_1$  and  $E_2$ ) of PBI molecules (**1**, 0.32mM and **2**, 0.282mM) before and after addition of  $CN^-$  (2.6mM). Experiments were carried out in dry THF under Argon atmosphere using  $[n-Bu_4]PF_6$  (129.05mM) as supporting electrolyte.

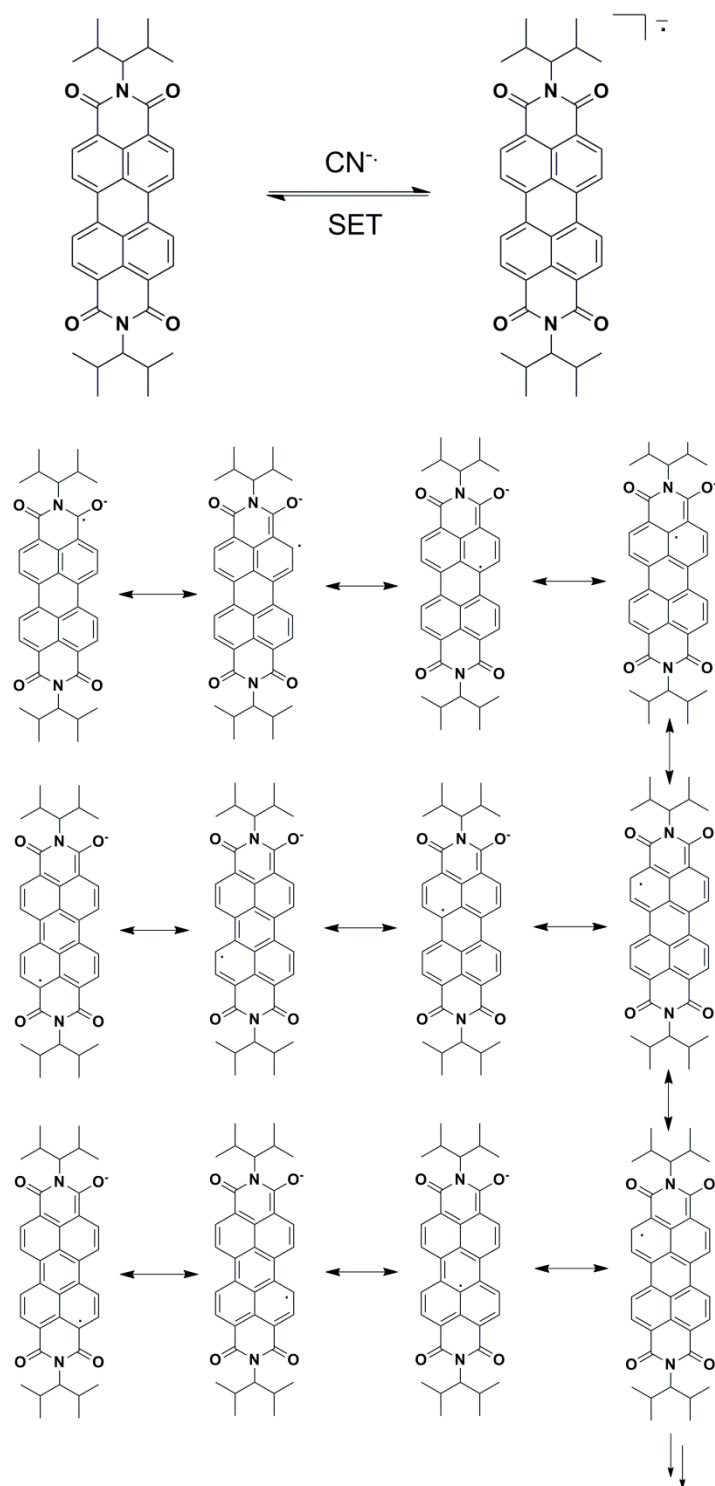


Fig. S6 Proposed Resonating Structures of PBI anion Radical