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Supplementary Information

Reversible Near-Infrared Fluorescence Switch by Novel Photochromic Unsymmetrical-Phthalocyanines Hybrids based on Bisthienylethene

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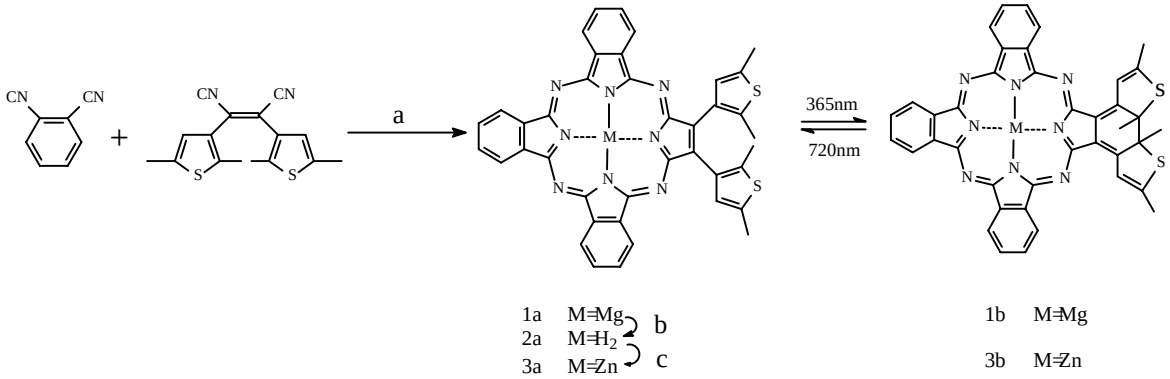

Scheme 1 Synthetic routines and photochromism of the BTE-uPcs. Reaction conditions: a, $Mg(OBu)_2$, n-BuOH, reflux, 24h; b, CH_3COOH, 50℃, 10h; c, $Zn(OAc)_2$, chlorobenzen/DMF, 100℃, 5h

A mixture of 1,2-dicyano-1,2-bis(2,5-dimethyl-3-thienyl)ethene (1.0 mmol) and much excessive 1,2-dicyanobenzene (100 mmol) were added to the $Mg(OBu)_2$ suspended in n-BuOH and the mixture was heated for 24h, turning dark blue/green. The solvent was evaporated out, and the residue was treated with $CHCl_3$. This solution was filtered to remove insoluble phthalocyanine (MgPc) byproduct. The residue was then purified twice

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by chromatography on silica gel using, at first $CHCl_3$ and then 2% EtOH in $CHCl_3$, and the major blue band was collected to get crude Mg(BTE-uPc)(1a) (yield 8 %). The magnesium atom is clearly removed using acetic acid at 50℃ for 10h to give H_2(BTE-uPc)(2a), which was purified by chromatography on silica gel (hexane/CH_2Cl_2(v/v): 1:1). Reaction of 2a with $Zn(OAc)_2$ in chlorobenzene/DMF (v/v: 2/1) proceeds smoothly at 100℃ for 5h to get Zn(BTE-uPc) (3a). Structural data of **1a (Mg(BTE-uPc))**: UV-Vis ($CHCl_3$) λ_{max}/ nm ($\varepsilon \times 10^{-5}/M^{-1}\,cm^{-1}$) : 678 (1.33), 653 (0.87), 448 (0.22), 353 (0.86). TOF-MS: calculated for $C_{40}H_{26}N_8S_2Mg$: 706.8 found: 707.1 (M^+). Element analysis: calculated C 67.97; H 3.68; N 15.85; found C 67.80; H 3.66; N 15.80 %. Emission ($CHCl_3$): λ_{max}/ nm (excited at λ / nm): 701(365), 703 (445). **2a (H_2(BTE-uPc))**: UV-Vis($CHCl_3$) λ_{max}/ nm ($\varepsilon \times 10^{-5}/M^{-1}cm^{-1}$): 703(1.24), 610(0.97), 564(0.24), 344(0.86). TOF-MS: calculated for $C_{40}H_{28}N_8S_2$: 684.5, found: 685.1 (M^+) ^{1}H NMR ($CDCl_3$)(δ ppm): -0.86(s, 2H, =NH), 2.38(s, 6H, -CH_3), 2.70(s, 6H, -CH_3), 5.05(s, 2H, thienyl aromatic proton). 7.75-9.2(m, 12h, fused benzene proton). Element analysis: calculated C 70.19; H 4.09; N 16.36; found C 70.11; H 4.10; N 16.30 %. **3a (Zn(BTE-uPc))**: UV-Vis ($CHCl_3$) λ_{max}/ nm ($\varepsilon \times 10^{-5}/M^{-1}cm^{-1}$): 678(1.20), 650(0.86), 597(0.23), 445(0.11), 353(0.56). TOF-MS: calculated for $C_{40}H_{26}N_8S_2Zn$: 747.9, found; 747.3(M^+), ^{1}H NMR($CDCl_3$)(δ ppm): 2.27(s, 6H, -CH_3), 2.52(s, 6H, -CH_3), 5.12(s, 2H, thienyl aromatic proton). 7.50-9.00(m, 12h, fused benzene proton). Element analysis: calculated C 64.24; H 3.48; N 14.97; found C 64.20; H 3.46; N 14.90 %. Emission($CHCl_3$): λ_{max}/ nm (excited at λ / nm): 701(365), 703(445).

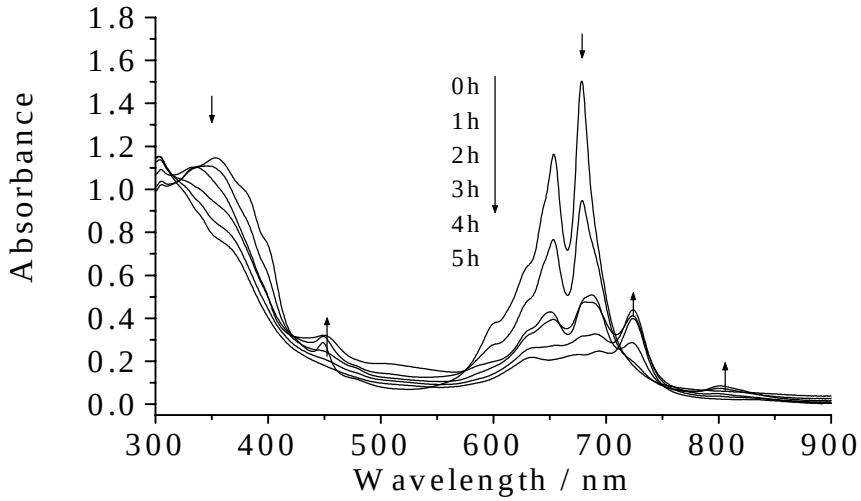

Fig. 1 Absorption spectra of compound 1a in $CHCl_3$ (1.3×10^{-5} M) and the changes in absorption of 1a under different irradiation time by light of 365 nm.

Absorption
2a
N
H
S