

Luminescent logic function of a surfactant-encapsulated polyoxometalate complex

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Instruments:

UV-vis spectroscopic measurement was carried out on a Shimadzu UV 3100PC spectrometer at ambient condition. The emission spectra were measured by a RF-5301PC spectrometer. The element analysis was performed on a Flash EA1112 from ThermoQuest Italia S.P.A. FT-IR spectra were obtained on a Bruker IFS66V FT-IR spectrometer equipped with a DGTS detector for the solid-state SEC-1 (KBr, 32 scans). The spectra were recorded with a resolution of 4 cm⁻¹. ¹H NMR spectra (TMS) were recorded on a Bruker UltraShield 500 MHz spectrometer. Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer TG/DTA-7 instrument and the heating rate is 10 °C min⁻¹.

Synthesis of materials:

1. Na₉EuW₁₀O₃₆·32H₂O (POM-1)

It was prepared and confirmed according to a published procedure.¹

2. Didodecyldimethylammonium bormide (DDDA)

N, N-dimethyldodecylamine (2.13 g, 10 mmol) and 1-bromododecane (2.49 g, 10 mmol) were dissolved in 50 ml ethanol and heated to reflux for 24 h. The mixture was concentrated to 5 ml, and then 50 ml cold diethyl ether was added to the concentrated solution dropwise. After storing at 0 °C for 3 days the white precipitate formed was filtered and washed with diethyl ether to give the product (A) in yield 91%. ¹H NMR (500 MHz, CDCl₃, relative to TMS): δ (ppm) = 3.53-3.50 (t, 4H, -(CH₂)₂N-), 3.40 (s, 6H, (CH₃)₂N-), 1.73-1.67 (m, 4H, 2-CH₂CH₂N), 1.40-1.26 (m, 36H, 2-(CH₂)₉-),

0.90-0.87 (t, 6H, 2CH₃CH₂-). Elemental analysis calcd (%) for C₂₆H₅₆NBr (462.64): C 67.50, H 12.20, N 3.03; found C 67.85, H 12.63, N 2.96.

3. *trans*-4-(4'-pyridylethenyl)phenol (A)

It was prepared according to literature procedures.² ¹H NMR (500 MHz, DMSO, TMS): δ (ppm) = 12.95 (s, 1H, -OH), 8.59 (d, 2H, *J* = 5.5 Hz, pyridyl), 7.98 (d, 2H, *J* = 8.5 Hz, phenyl), 7.78 (d, 2H, *J* = 5.5 Hz, pyridyl), 7.64 (d, 1H, *J* = 16.5 Hz, -CH=CH-), 7.61 (d, 2H, *J* = 8.5 Hz, phenyl), 7.42 (d, 1H, *J* = 16.5 Hz, -CH=CH-).

4. 10-[*trans*-4-(4'-pyridylethenyl)phenol]decyl bromide (B)

1,10-Dibromodecane (2.7 g, 9 mmol), A (1.86 g, 9 mmol) and potassium carbonate (2.69 g, 18 mmol) were added in 40 mL of dimethylformamide (DMF). The mixture was stirred at room temperature for 2 days. The reaction mixture was poured into ice water and filtered. The precipitate was dried and treated with dichloromethane. The insoluble solid was filtered off and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography using silica gel (100-200 mesh) with dichloromethane/diethyl ether (10:1, v/v) as eluent to give the product (B). Yield: 42.5%. ¹H NMR (500 MHz, CDCl₃, TMS): δ (ppm) = 8.55 (d, 2H, *J* = 5.5 Hz, pyridyl), 7.47 (d, 2H, *J* = 8.5 Hz, phenyl), 7.36 (d, 2H, *J* = 5.5 Hz, pyridyl), 7.28 (d, 1H, *J* = 16.5 Hz, -CH=CH-), 6.92 (d, 2H, *J* = 8.5 Hz, phenyl), 6.89 (d, 1H, *J* = 16.5 Hz, -CH=CH-), 3.98 (t, 2H, *J* = 6.5 Hz, -OCH₂-), 3.52 (m, 4H, -CH₂N), 3.42 (s, 6H, N(CH₃)₂), 1.79 (m, 2H, -CH₂-), 1.70 (m, 4H, -CH₂-), 1.25-1.50 (m, 28H, -(CH₂)₁₄-), 0.88 (t, 3H, *J* = 9.0, -CH₃).

5. 10-[*trans*-4-(4'-pyridylethenyl)phenol]decyldodecyldimethylammonium bromide (PyC₁₀C₁₂N)

N,N-Dimethyldodecylamine (2.77 g, 13 mmol) and B (0.41 g, 1.3 mmol) were dissolved in 15 mL of dichloromethane. The mixture was stirred at room temperature for 7 days. After most of solvent was evaporated under reduced pressure, Et₂O (20 mL) was added into the residue and the resulted precipitate was filtered. The precipitate was purified by column chromatography using silica gel (100-200 mesh) with dichloromethane/methanol (25:1, v/v) as eluent to give the product PyC₁₀C₁₂N. Yield: 70.1%. ¹H NMR (500 MHz, CDCl₃, TMS): δ (ppm) = 8.55 (d, 2H, *J* = 8.55 Hz,

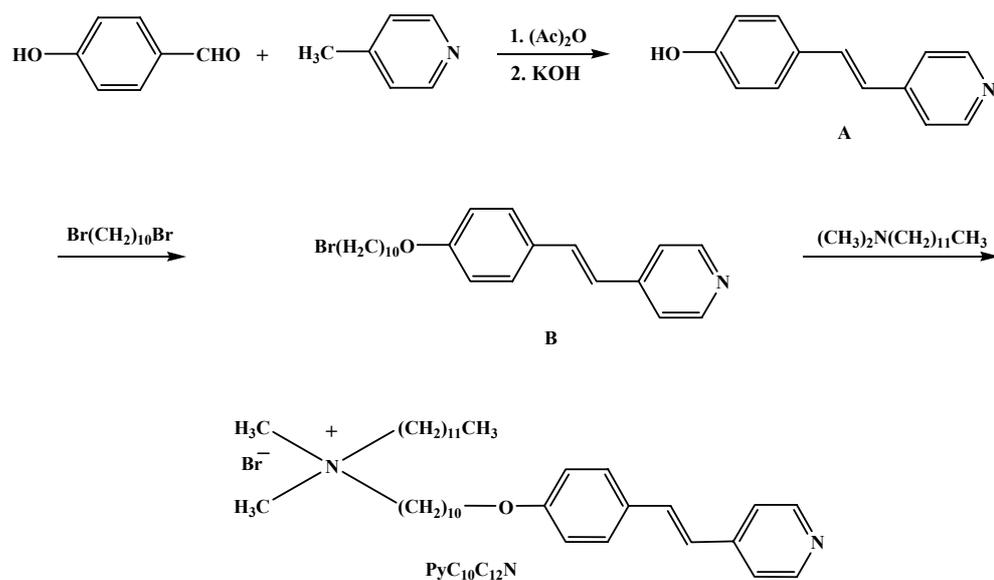
pyridyl), 7.47 (d, 2H, $J = 8.5$ Hz, phenyl), 7.36 (d, 2H, $J = 5.5$ Hz, pyridyl), 7.28 (d, 1H, $J = 16.5$ Hz, -CH=CH-), 6.92 (d, 2H, $J = 8.5$ Hz, phenyl), 6.89 (d, 1H, $J = 16.5$ Hz, -CH=CH-), 3.98 (t, 2H, $J = 6.5$ Hz, -OCH₂-), 3.52 (m, 4H, -CH₂N), 3.42 (s, 6H, N(CH₃)₂), 1.79 (m, 2H, -CH₂-), 1.70 (m, 4H, -CH₂-), 1.25-1.50 (m, 28H, -(CH₂)₁₄-), 0.88 (t, 3H, $J = 9.0$, -CH₃). Elemental analysis calcd (%) for C₃₇H₆₀ON₂Br·H₂O (647.81): C 68.70, H 9.66, N 4.33; found: C 69.05, H 10.10, N 4.39.

6. SEC-1

The molar ratio of surfactant PyC₁₀C₁₂N and DDDA was fixed at 4:5 for encapsulating POM-1. POM-1 was dissolved in aqueous solution (pH = 6.0) and then a chloroform solution containing the two surfactants in a defined ratio was added with stirring. The initial molar ratio of total surfactants to POM-1 was controlled at 9:1.13. The organic phase was separated and the SEC-1 was obtained by evaporating the chloroform to dryness. Then the product was further dried in vacuum until the weight remained constant. ¹H NMR (500 MHz, CDCl₃, TMS): δ (ppm) = 8.55 (d, 8H, $J = 8.55$ Hz, pyridyl), 7.47 (d, 8H, $J = 8.5$ Hz, phenyl), 7.36 (d, 8H, $J = 5.5$ Hz, pyridyl), 7.28 (d, 4H, $J = 16.5$ Hz, -CH=CH-), 6.92 (d, 8H, $J = 8.5$ Hz, phenyl), 6.89 (d, 4H, $J = 16.5$ Hz, -CH=CH-), 3.96 (t, 8H, $J = 6.5$ Hz, -OCH₂-), 3.15-2.90 (br, 54H, -CH₂N), 2.61-2.31 (br, 36H, NCH₃), 1.80-1.15 (br, 344H, -CH₂-), 0.88 (t, 42H, $J = 9.0$, -CH₃). IR (KBr, cm⁻¹): ν_{as} (O-H) 3406, ν_{as} (CH₂) 2924, ν_{s} (CH₂) 2852, ν_{as} (C=C) 1633, ν (C₆H₅N) 1591, ν (C₆H₅) 1514, δ (CH₂) 1467, δ (CH-N⁺) 1419, ν_{as} (C₆H₅-O-C) 1256, ν_{s} (C₆H₅-O-C) 1024, ν_{as} (W-O_d) 938, 924, ν_{as} (W-O_c-W) 838, 806, 773. Elemental analysis calcd (%) for SEC-1 C₂₇₈H₅₂₄N₁₃O₄₂EuW₁₀ (6711.56): C 49.75, H 7.87, N 2.71; found: C 50.20, H 8.22, N 2.68. The thermogravimetric analysis (TGA) stage of SEC-1 (temperature range: 20 to 200°C) corresponds to the loss of the crystalline water (0.8%), and the calculated number of crystalline water is about 2. Combining the TGA and elemental analysis, SEC-1 should correspond to the formula (PyC₁₀C₁₂N)₄(DDDA)₅EuW₁₀O₃₆·2H₂O.

(1) M. Sugeta and T. Yamase, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 444.

(2) V. W. Yam, Y. Yang, H. Yang and K. Cheung, *Organometallics*, 1999, **18**, 5252.



Scheme S1. The schematic synthetic path of the surfactant $\text{PyC}_{10}\text{C}_{12}\text{N}$.

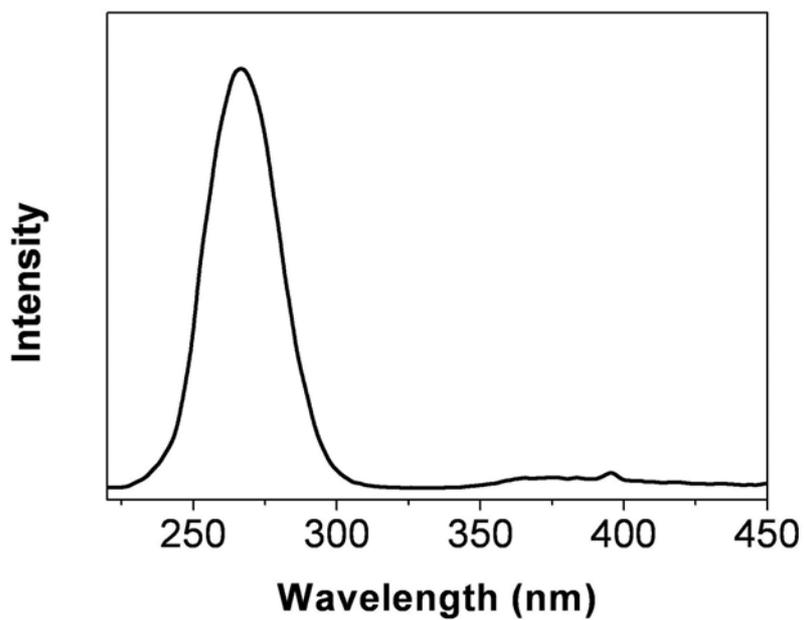


Figure S1 The excitation spectrum of SEC-1 in CH_2Cl_2 , monitored at 614 nm.

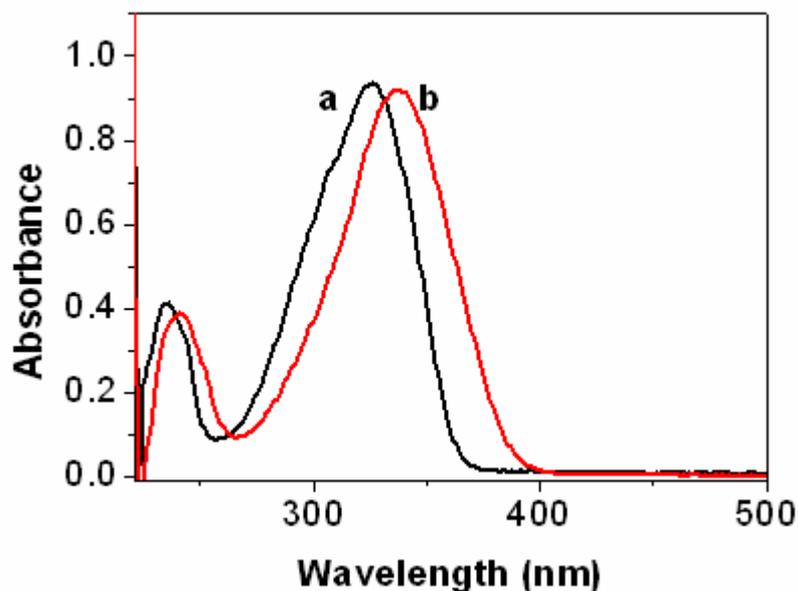


Figure S2 UV-Vis spectra of (a) pure PyC₁₀C₁₂N in CH₂Cl₂ (5.5×10^{-5} mol/L) (b) PyC₁₀C₁₂N in CH₂Cl₂ (5.5×10^{-5} mol/L) after the addition of ZnCl₂ (2:1 PyC₁₀C₁₂N/ZnCl₂).

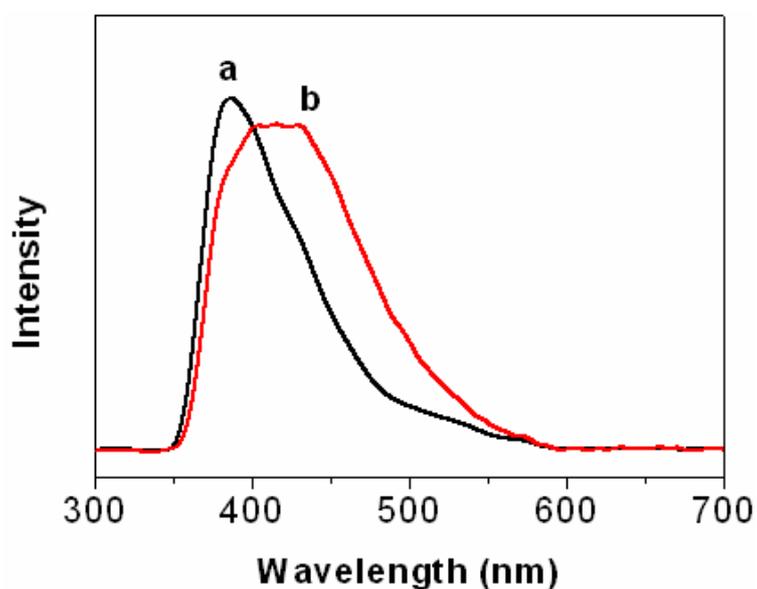


Figure S3 Emission spectra of (a) pure PyC₁₀C₁₂N in CH₂Cl₂ (5.5×10^{-5} mol/L) and (b) PyC₁₀C₁₂N in CH₂Cl₂ (5.5×10^{-5} mol/L) after the addition of ZnCl₂ (2:1 PyC₁₀C₁₂N/ZnCl₂), excited at 260 nm.