Supplementary data

Soft Mimic Gear-Shift with a Multi-stimulus Modified Diarylethene

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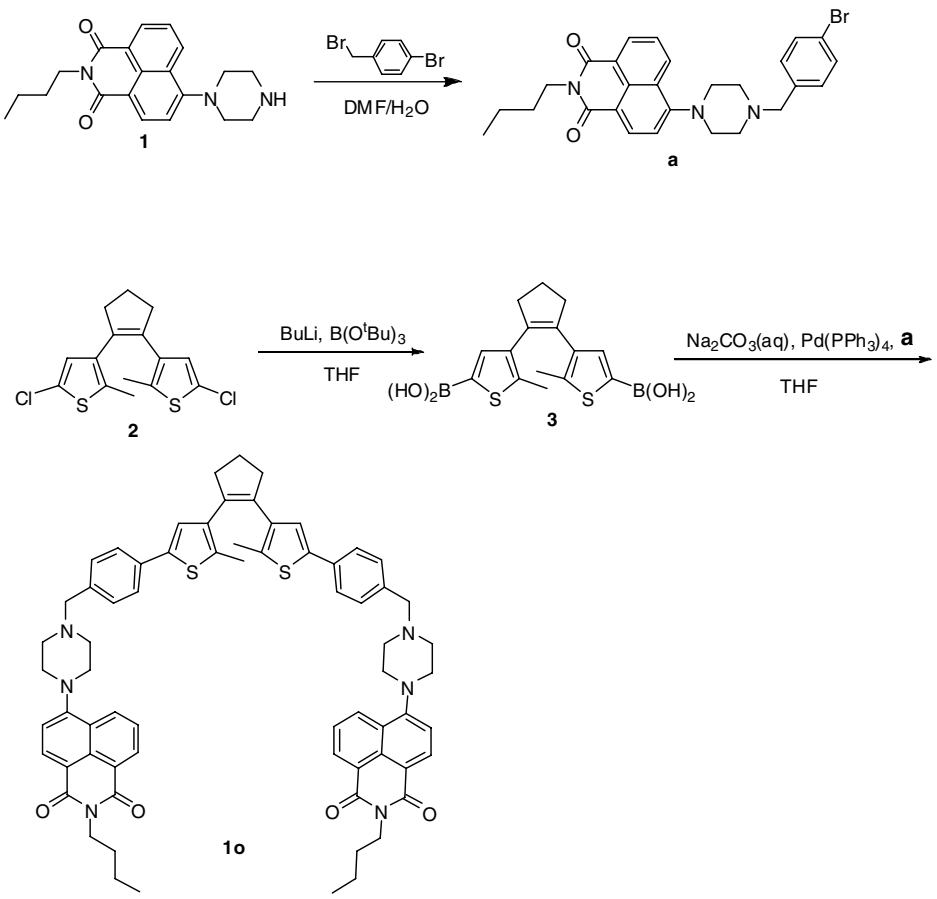
General procedure:

^{1}H NMR spectra were recorded on a Bruker AM 400 spectrometer with tetramethyl silane (TMS) as internal reference. MS were recorded on EI or ESI mass spectroscopy. Absorption spectra were measured on a Varian Cary500 UV-Vis spectrophotometer. Fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer. The optical switch experiments were carried out using a photochemical reaction apparatus with a 200W Hg lamp.

Materials:

Reagents and starting materials were used as received. Solvents were distilled and dried before use. Compound **1** and **2** were synthesized and purified according to the established procedure[1-2].

Synthesis：



Scheme S1: Synthesis route of Nap-Pip-DTE **1o**.

4-(4-(4-bromobenzyl)piperazin-1-yl)-N-butyl-1,8-naphthalimide (**a**)

Compound **1** (5.0g, 0.015mol), 1-bromo-4-(bromomethyl)benzene (4.13g, 0.0165mol) and K_2CO_3 (10.35g, 0.075mol) were mixed together and stirred in DMF/H_2O (10:1, 15ml) at 50˚C for 8 hours. The reactive mixture was poured into water and filtered to yield yellowish powder. This yellowish powder was purified by column chromatography on silica (dichloromethane–ethyl acetate = 10 : 1 v/v) to yield compound **a** (6.46 g), yield 86 %. ^{1}H NMR (400MHz, $CDCl_3$, ppm): 8.58 (d, 1H, naphthalimide C-H), 8.51 (d, 1H, naphthalimide C-H), 8.40 (d, 1H, naphthalimide C-H), 7.68 (t, 1H, naphthalimide C-H), 7.49 (q, 2H, benzyl C-H), 7.26 (q, 2H, benzyl C-H), 7.21 (d, 1H, napthalin C-H), 4.17 (t, 2H, -CH_2-), 3.61 (s, 2H, -CH_2-), 3.29 (s,

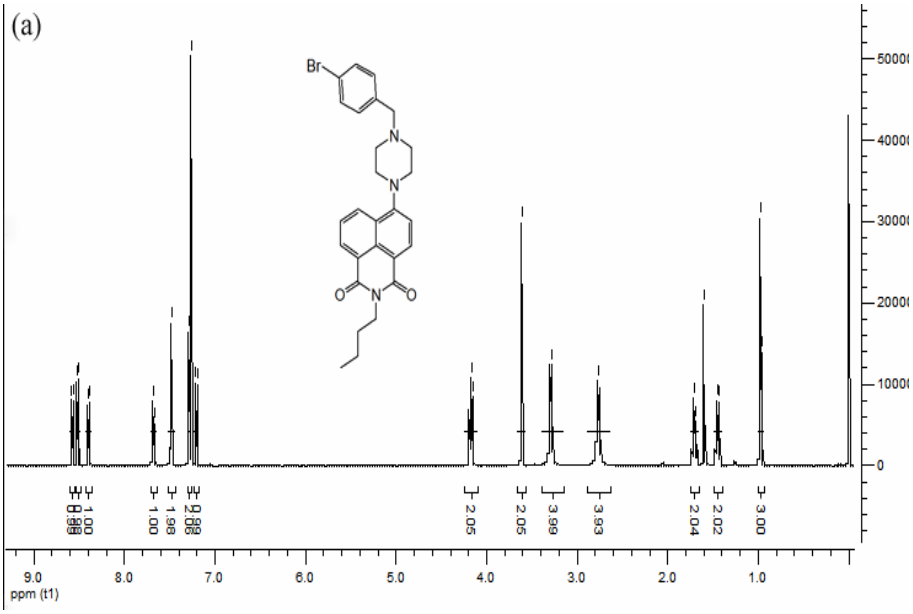
4H, piperazin -CH_2-), 2.76 (s, 4H, piperazin –CH_2-), 1.70 (m, 2H, -CH_2-), 1.44 (m, 2H, -CH_2-), 0.97 (t, 3H, -CH_3). ^{13}C NMR (400 MHz, $CDCl_3$): δ164.506, 164.044, 155.897, 136.913, 132.525, 131.486, 131.055, 130.806, 130.219, 129.848, 126.140, 125.616, 123.300, 121.099, 116.771, 114.905, 62.294, 53.100, 53.044, 40.095, 30.268, 20.419, 13.897. TOF MS ES$^+$: calculated for ($C_{27}H_{29}N_3O_2Br$) 505.14, found: 506.1431 (M^+H).

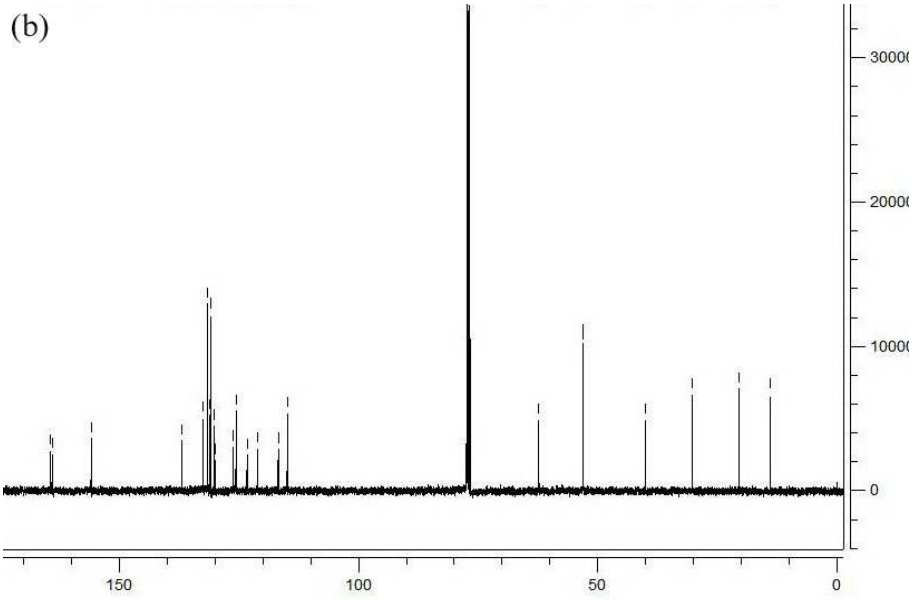
1,2-bis(5-(4-(N-butyl-1,8-naphthalimide-4-piperazinyl)benzyl)-2-methyl-3-thienyl)cyclopentene (1o)

To a stirred solution of 1,2-bis(5-cholo-2-methyl-3-thienyl)cyclopentene **2** (1 g, 3 mmol) in THF (20 ml) at -78˚C under Ar in the absence of light was added dropwise 2.5 M n-BuLi in hexane (0.39 g, 6 mmol), and the reaction mixture was stirred at -70˚C for further 30 min. Then tributyl borate (1.38 g, 6 mmol) was quickly added in one portion. This reddish solution was stirred for 1 h at room temperature, and was then used in the Suzuki cross coupling reaction without any workup because the product is deboronized during isolation.

A mixture of compound **a** (3g, 6mmol), the catalyst Pd (PPh_3)$_4$ and THF (10ml) was stirred for 15 min at room temperature. Then aqueous Na_2CO_3 (8mL, 2 M) was added. The reactive mixture was heated at a temperature of 60˚C, and the solution of bis(boronic) esters prepared from 1,2-bis(5-cholo-2-methyl-3-thienyl)cyclopentene was added dropwise via a syringe. Subsequently, the mixture was refluxed for 24h and cooled to room temperature. The reactive mixture was poured into H_2O and extracted with ether, and the organic layer was collected and dried with anhydrous $MgSO_4$. After concentration, the compound was purified by column chromatography on silica (dichloromethane–ethyl acetate = 5 : 1 v/v) to yield compound **1o** (1.18 g), yield 35 %.^{1}H NMR (400MHz , $CDCl_3$, ppm) : 8.57 (d, 2H, naphthalimide C-H), 8.50 (d, 2H, naphthalimide C-H), 8.40 (d, 2H, naphthalimide C-H), 7.67 (t, 2H, naphthalimide C-H), 7.48 (d, 4H, benzyl C-H), 7.35 (d, 4H, benzyl C-H), 7.21 (d, 2H, naphthalimide C-H), 7.05 (s, 2H, thienyl C-H), 4.16 (t, 4H, -CH_2-), 3.65 (s, 4H,

-CH_2-), 3.29 (s, 8H, piperazin –CH_2-), 2.85 (t, 4H, -CH_2-), 2.78 (s, 8H, piperazin –CH_2-), 2.09 (m, 2H, -CH_2-), 2.00 (s, 6H, -CH_3), 1.70 (m, 4H, -CH_2-), 1.44 (m, 4H, -CH_2-), 0.97 (t, 6H, -CH_3). ^{13}C NMR (400 MHz, $CDCl_3$): δ164.470, 164.004, 155.934, 139.395, 136.728, 136.551, 134.652, 134.434, 133.617, 132.504, 131.015, 130.235, 129.830, 129.692, 126.111, 125.570, 125.257, 123.951, 123.270, 116.685, 114.863, 62.686, 53.115, 53.069, 40.083, 38.518, 30.275, 23.035, 20.425, 14.489, 13.906. TOF MS ES$^+$: calculated for ($C_{69}H_{71}N_6O_4S_2$) 1110.49, found: 1111.4974 (M^+H).





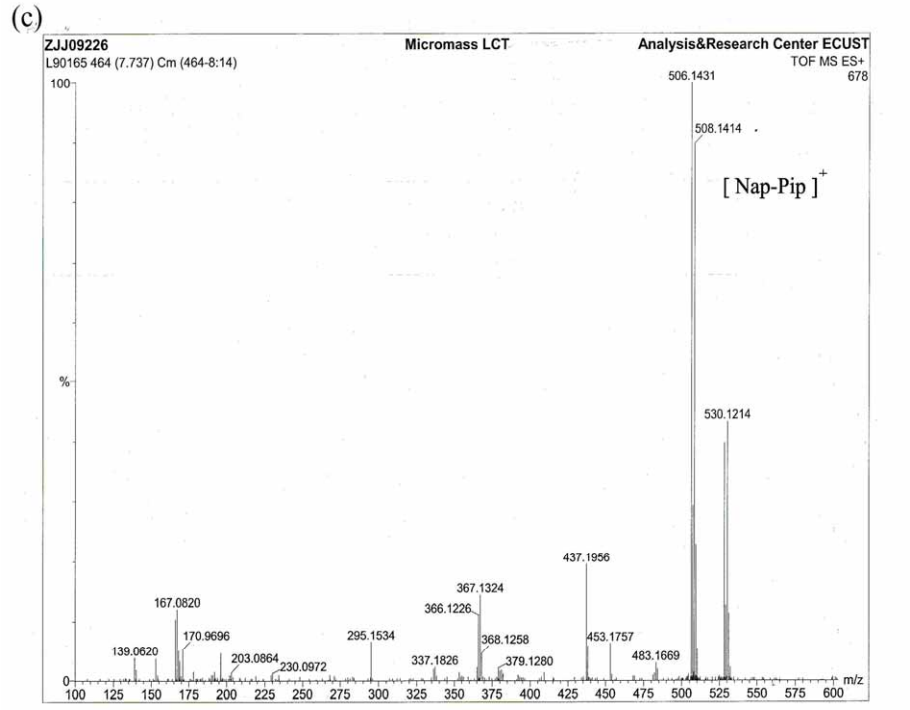
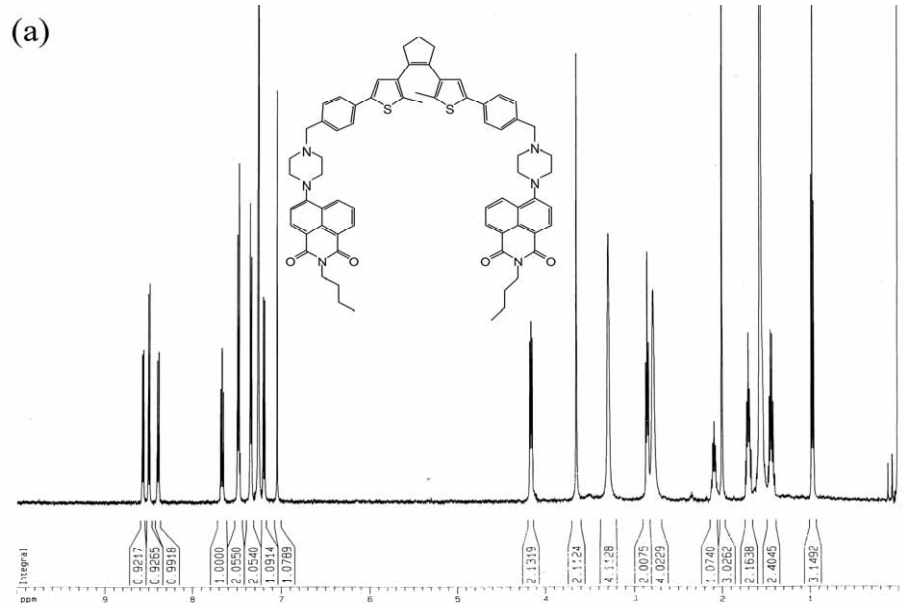


Figure S1: (400MHz) (a) ^{1}H-NMR spectra (b) ^{13}C-NMR spectra and (c) ESI-MS spectra of Nap-Pip (**a)** in $CDCl_3$, and calculated isotopic distribution for the peaks at 506.1431.



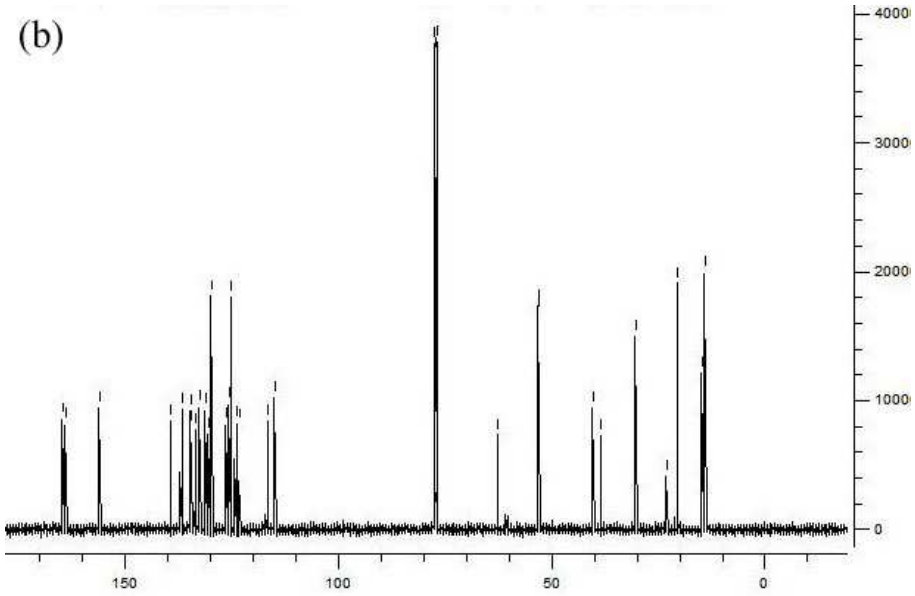
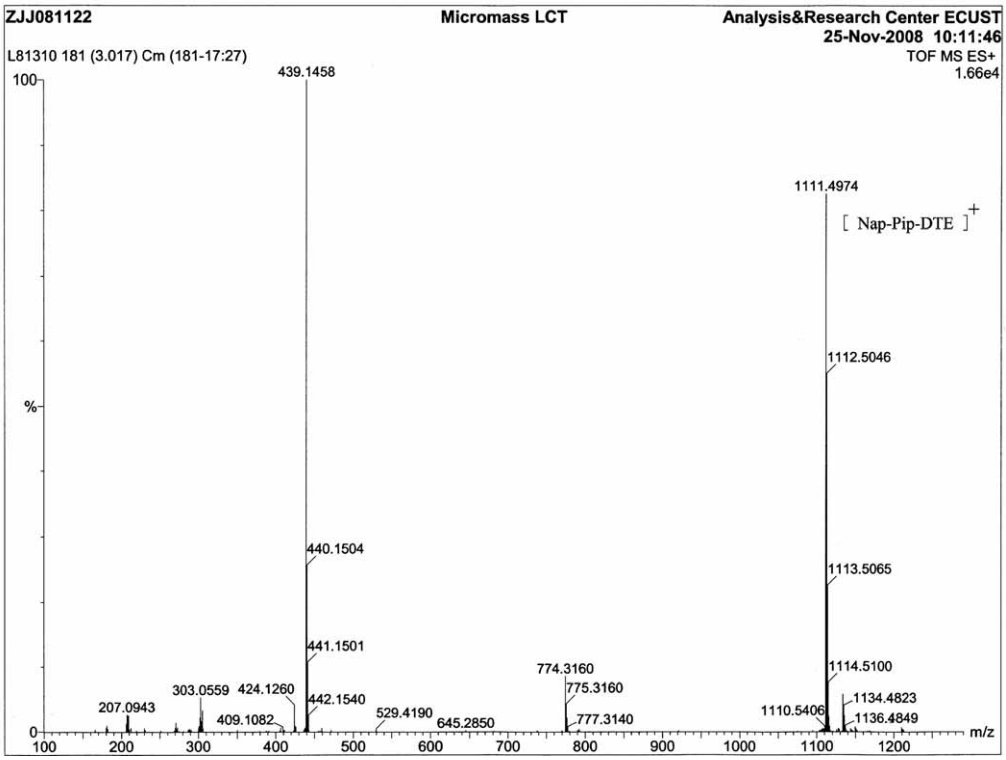


Figure S2: (400MHz) (a) ^{1}H-NMR spectra (b) ^{13}C-NMR spectra of Nap-Pip-DTE **1o** in $CDCl_3$.



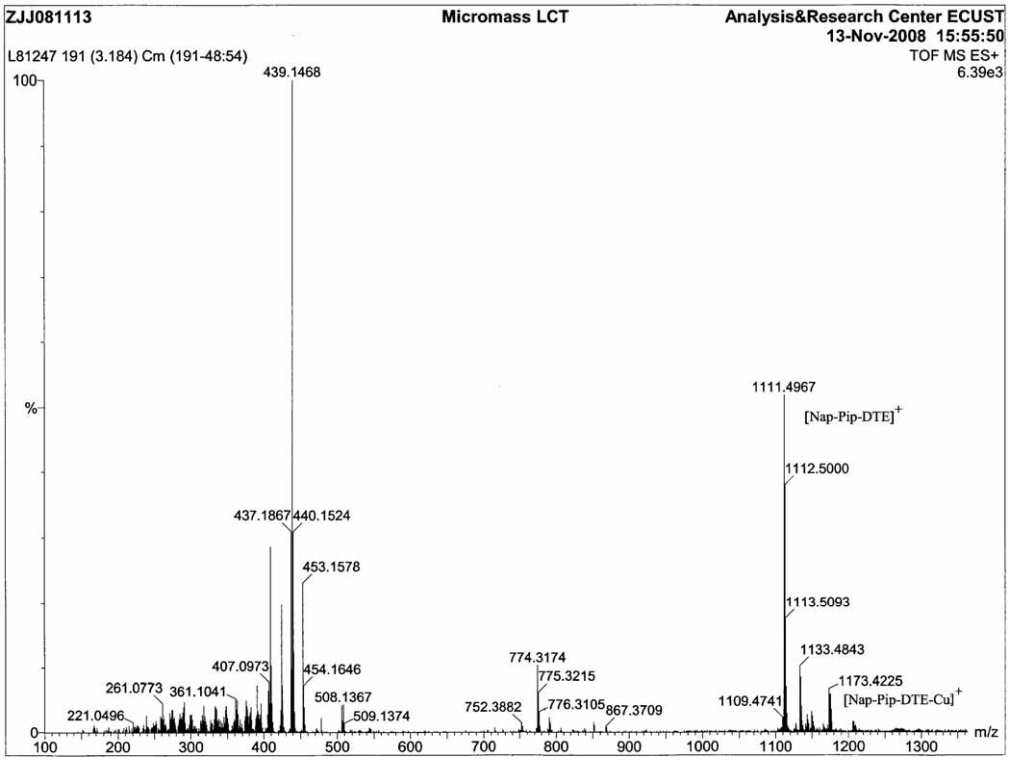


Figure S3: ESI-MS spectra of Nap-Pip-DTE **1o** (top) and Nap-Pip-DTE-Cu **1oCu** (bottom) in a mixture of H_2O-CH_3CN (1:9, v/v), and calculated isotopic distribution for the peaks at 1111.4974 and 1173.4255, respectively.

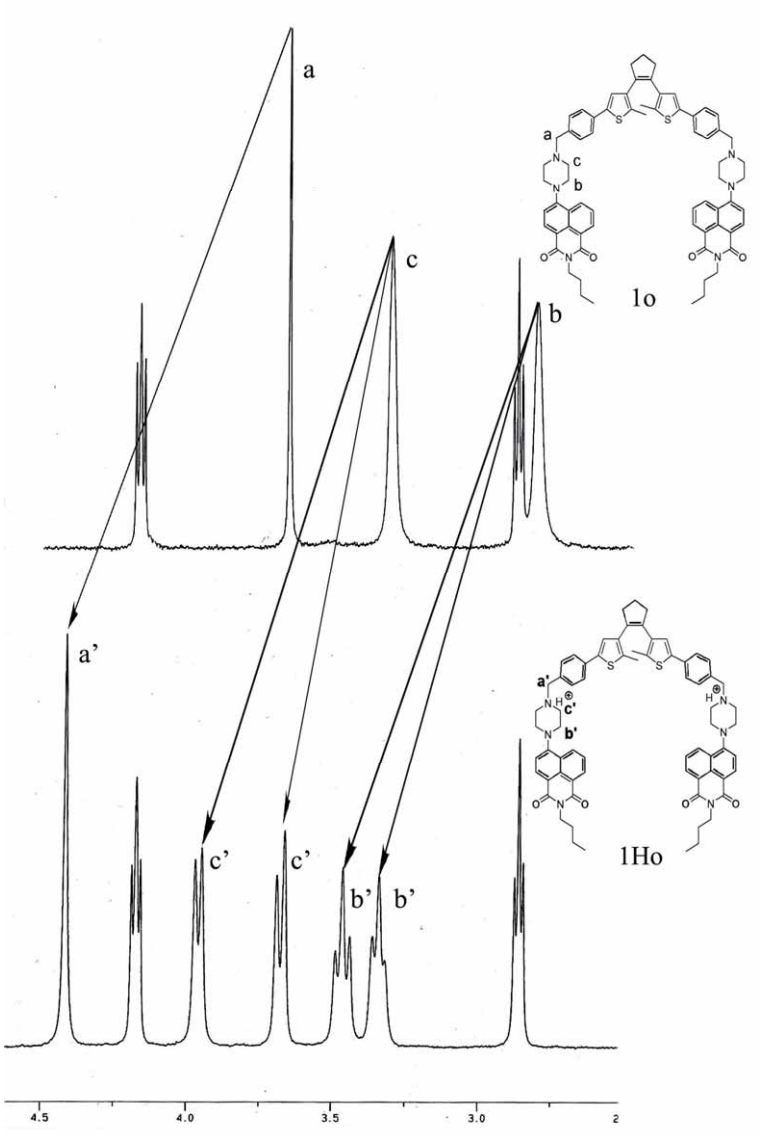


Figure S4: Parts of the ^{1}H NMR spectra of: Nap-Pip-DTE **1o** (top) and after protonation **1Ho** (bottom) in $CDCl_3$.

^{1}H NMR studies of protonation of Nap-Pip-DTE **1o** give useful information consistent with the above analysis (Figure S4). The peak at around δ = 3.65 ppm (a), which was assigned to methylene protons in unprotonated **1o**, shift significantly downfield to around δ = 4.42 ppm (a') upon protonation. The signals of the protons of piperazine moieties also underwent a remarkable downfield shift from δ = 2.78 (c)

to . = 3.34 and 3.47 (c'), and from . = 3.29 (b) to . = 3.96 and 3.73 (b'). These deshielding effects confirm the protonation form of Nap-Pip-DTE-H **1Ho**.

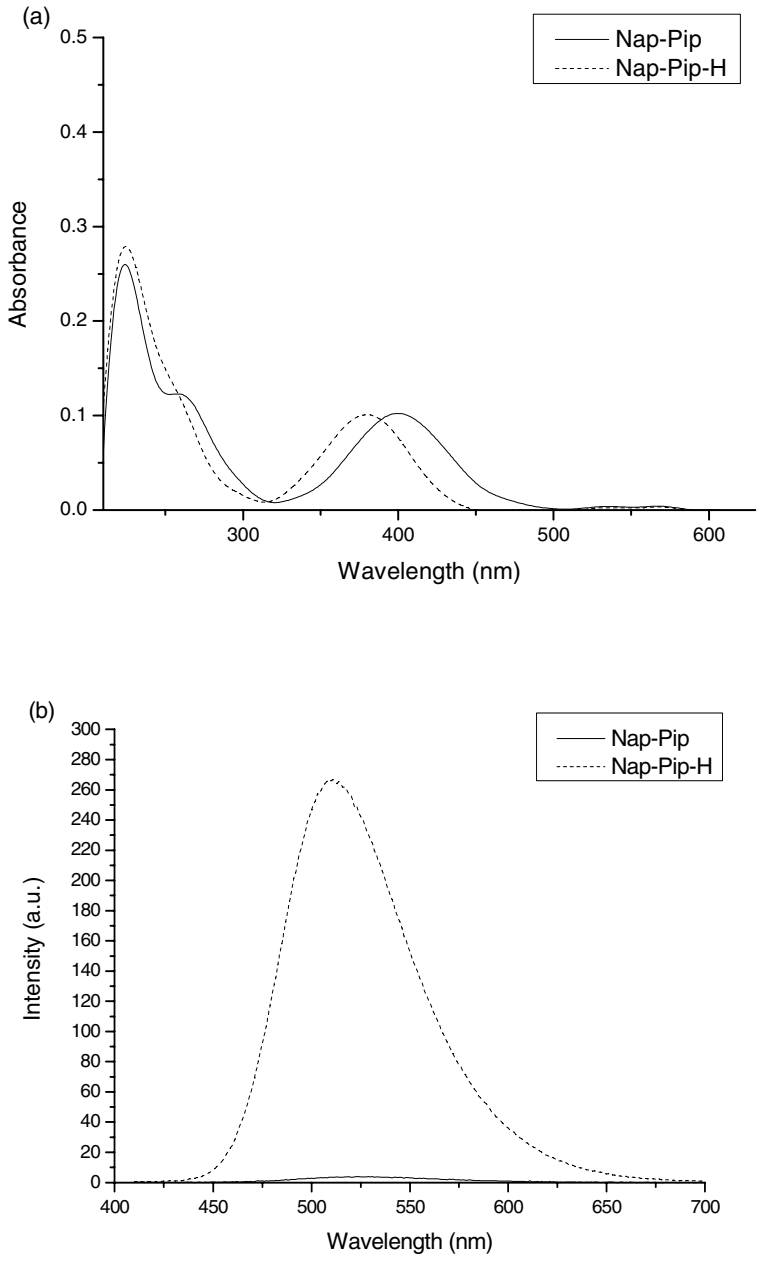


Figure S5: (a) Absorption spectra and (b) emission spectra of Nap-Pip (10^{-5} M, solid line) and Nap-Pip-H (10^{-5} M, dash line) in a mixture of CH_3CN: H_2O = 9:1 (v/v). All emissions are excited upon 400 nm at 298K.

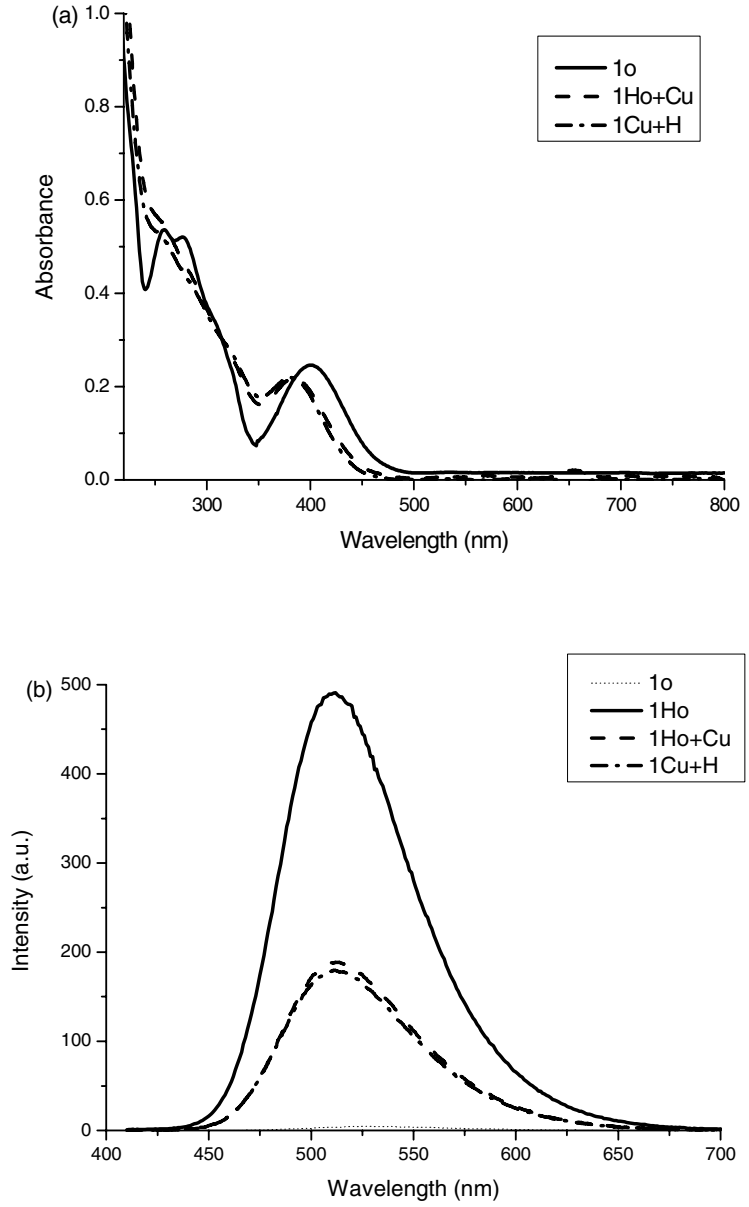


Figure S6: (a) Absorption spectra and (b) emission spectra of **1Ho+Cu** (10^{-5} M, dash line) and **1oCu+H** (10^{-5} M, dash dotted line) in a mixture of CH_3CN: H_2O = 9:1 (v/v). All emissions are excited upon 400 nm at 298K.

From Figure S6 we can evidently see that the absorption and emission spectra of **1Ho+Cu** (first protonation then complexed with Cu^{2+}) and **1oCu+H** (first complexed with Cu^{2+} then protonation) are almost totally overlapped. Thus conclusion can be drawn that there are no sequence-ordered behavior in adding Cu^{2+} and protonation.

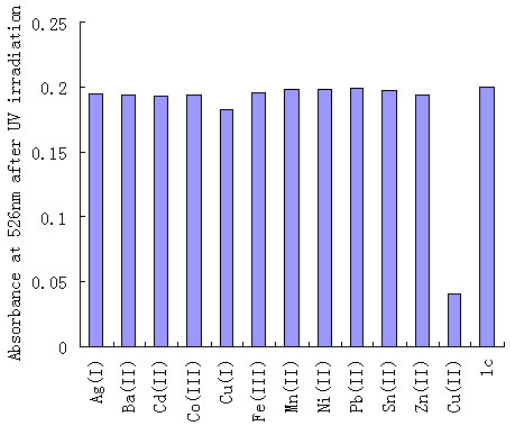
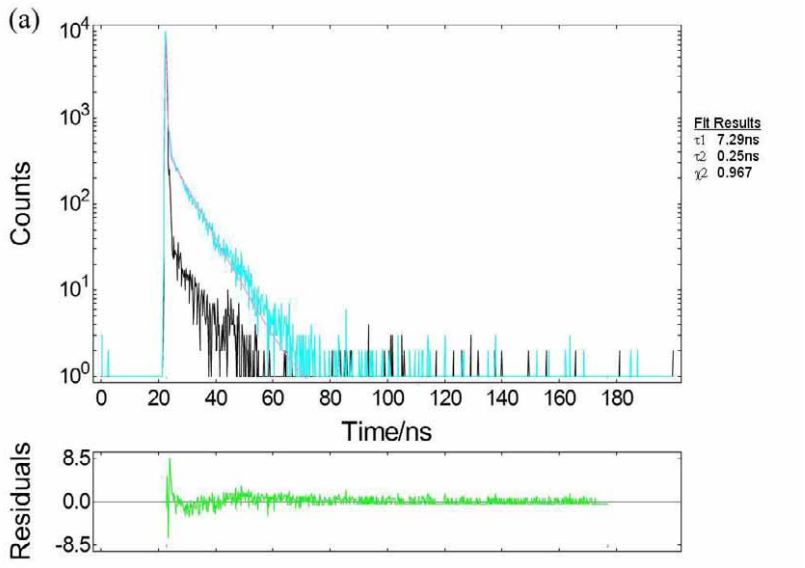


Figure S7: Selectivity of the complexation of Cu^{2+} ions depicted in Scheme 2. The concentration of all the metal ions was 0.01M.

Figure S7 depicts the absorbance at 526 nm after irradiation upon UV (254 nm) for Nap-Pip-DTE **1o** upon interaction with different metal ions. These results are almost the same with **1c** (closed form of Nap-Pip-DTE **1o**) except Cu (II) ion. Thus indicates that the Nap-Pip-DTE has selectivity in complexation with Cu (II) ion to form a molecular lock.



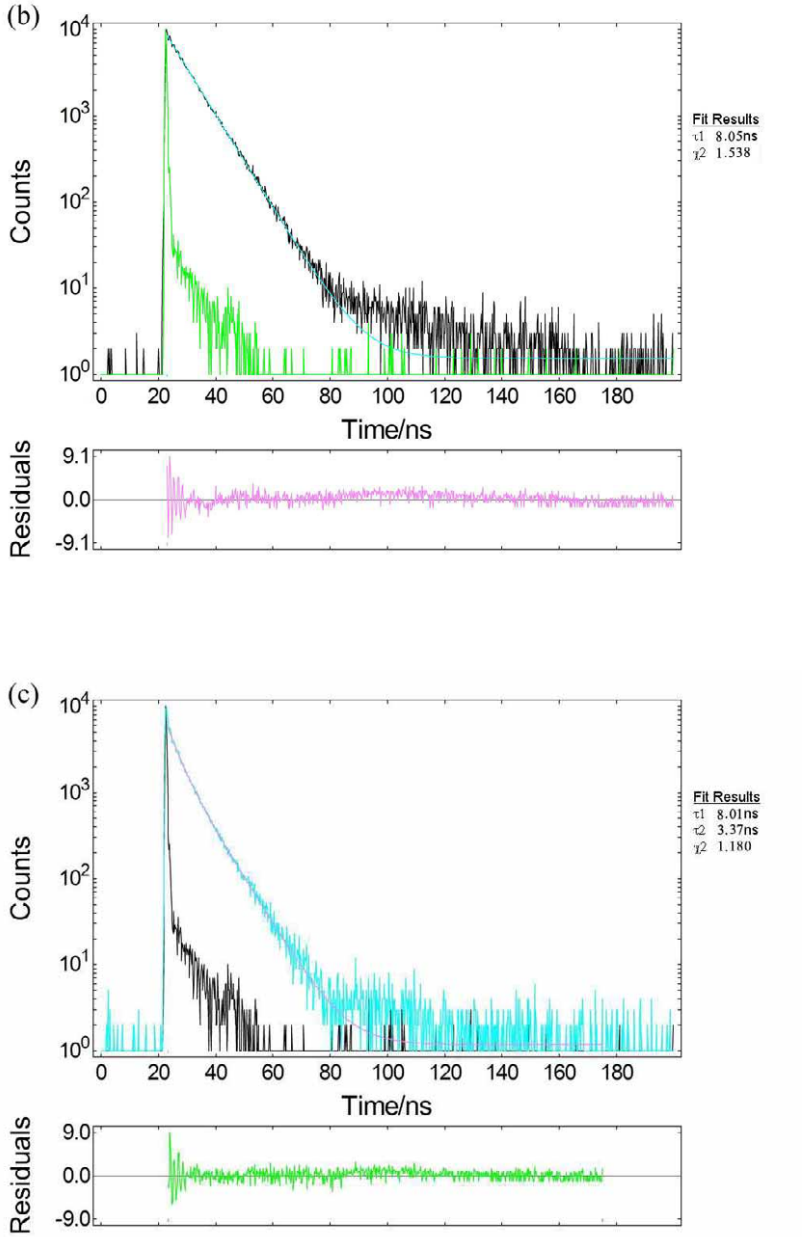


Figure S8: The fluorescence life-time of **1o**, **1Ho** and **1oCu** was measured in the mixture of CH_3CN: H_2O (v/v = 9:1) at 510 nm emission monitor upon excited at 440 nm at room temperature. (a) The life-time of **1o** (blue, 1 = 7.29 ns, 2 = 0.25 ns). (b) The life-time of **1Ho** (black, 1 = 8.05 ns). (c) The life-time of 1oCu (blue, 1 = 8.01 ns, 2 = 3.37 ns).

References:

1 B. Liu, H. Tian, *Chem. Commun.*, 2005, 3156.
2 (a) L. N. Lucas, J. J. D. de Jong, J. H. van Esch, R. M. Kellogg, B. L. Feringa, *Eur. J. Org. Chem.*, 2003, 155; (b) B. Qin, R. Yao, X. Zhao, H. Tian, *Org. Biomol. Chem.*, 2003, **1**, 2187.