Electronic Supplementary Information (ESI)

Efficient Energy Transfer between Coronene-Modified Permethyl-*β*-cyclodextrins and Porphyrin for Light Induced DNA Cleavage

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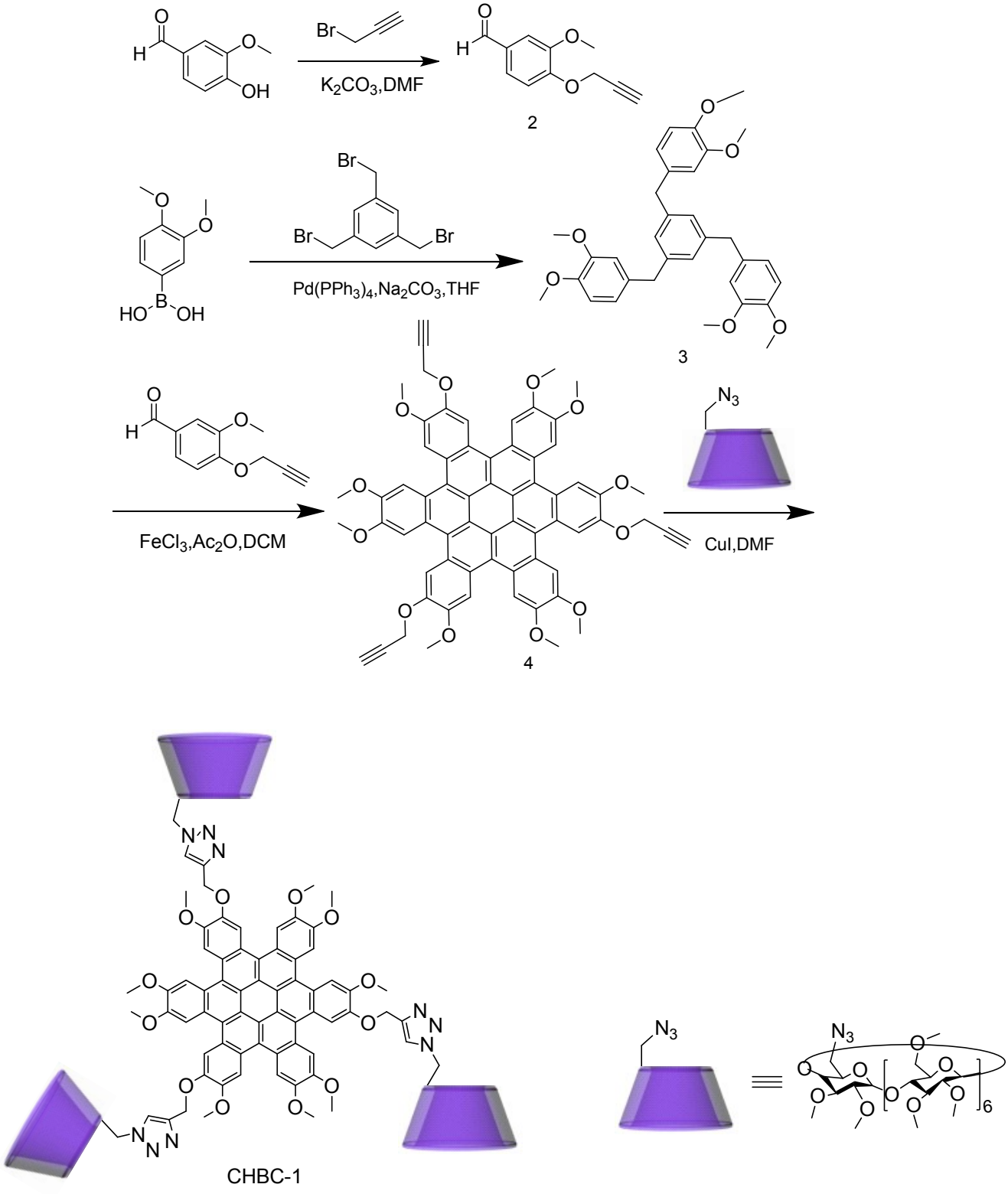
Materials: β-Cyclodextrin was purchased from Wako. CHBC and 6-deoxy-6-azido-permethyl-β-CD was prepared according to the literature procedure. Anhydrous CH_2Cl_2 and DMF were distilled from calcium hydride. Other chemicals and solvents were commercially available. The reaction was monitored using analytical thin layer chromatography (TLC, GF254). Column chromatography was performed on 200-300 mesh silica gel.

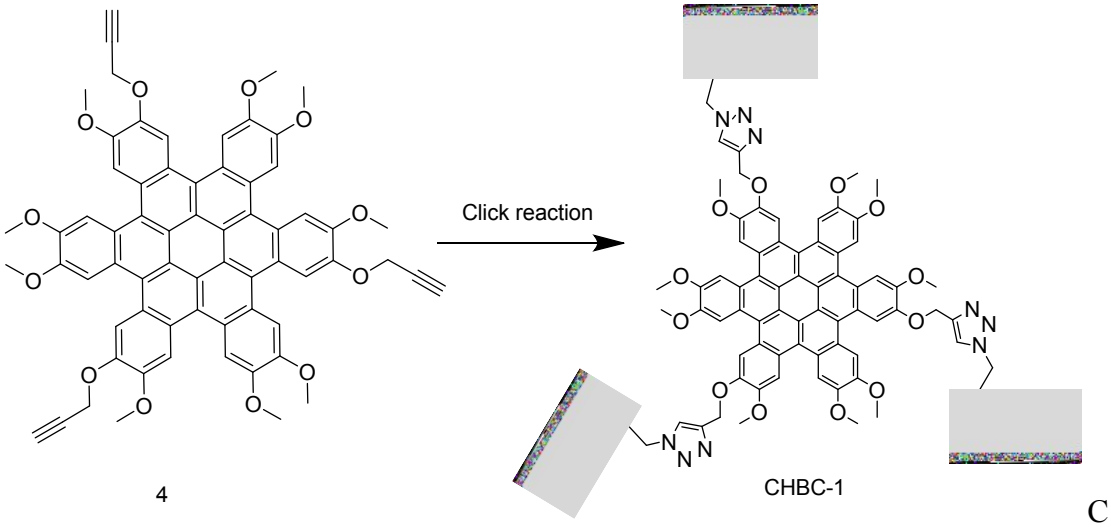
Measurements. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance spectrometers using $CDCl_3$ as a solvent. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. The mass spectra of the compounds were recorded on Varian 7.0T FTMS in positive-ion mode. UV/Vis spectra were recorded on Shimadzu UV-3600 spectrophotometerin a quartz cell (light path 10 mm) at 25 °C. Steady-state fluorescence spectra were recorded in a quartz cell (light path10 mm) using a Varian Cary Eclipse fluorescence spectrometer at 25°C. Induced circular dichroism spectra were collected on a BioLogic MOS500 spectro polarimeter in a quartz cell (light path 10 mm). Before examined on a laser lightscattering spectrometer (BI-200SM), the sample solution (3 mL) was filtered through a 0.45 μm Millipore filter into a clean scintillation vial. The light scattering spectrometer (BI-200SM) equipped with a digital correlator (Turbo Corr) at 636 nm at a scattering angle of 90°. The sample solution was dropped onto a copper grid and then air-dried. TEM images were acquired by a high-resolution transmission electron microscope (Philips Tecnai G2 20S-TWIN microscope) operating at an accelerating voltage of 200 keV. The sample for the SEM measurements werepreprepared by dropping the solution onto a copper grid, and then air-dried. The SEM images were recorded on a JEOL JSM-7500F scanning electronic microscope operating at an accelerating voltage of 30 keV. The fluorescence lifetimes were measured by steady/transient fluorescence spectrometer on a F900 LDH-P-C-375 instrument (Edinburg Instruments Ltd., Livingstone, UK) with pulsed laser diode.

1. Synthesis and characterization of the intermediates and the products

Synthetic routes of CHBC-1:



The procedure for the synthesis of CHBC-1



C

uI (146 mg, 0.77 mmol) was added to a solution of **4**[1](200 mg, 0.19 mmol) and 6-deoxy-6-azido-permethyl-β-CD (1.12 g, 0.77 mmol) in anhydrous DMF which was stirred at 80 °C for 48 h under argon. After cooling to room temperature, the mixture was filtered to remove any insoluble copper salt, and the filtrate was evaporated under reduced pressure to remove excess DMF. The residue was purified by chromatography to give CHBC-1 as a yellow solid (0.50 g, yield 48 %).^{1}H NMR (400 MHz, $CDCl_3$): 8.93 (d, J = 8.0 Hz, 3 H), 8.79-8.76 (m, 9 H), 7.90 (d, J = 8.0Hz, 3 H), 5.57 (m, 3 H), 5.50–5.40 (m, 3 H), 5.36 (m, 3 H), 5.22–5.05 (m, 16 H), 4.99–4.81 (m, 5 H), 4.37–2.88 (m, 330 H).^{13}C NMR (100 MHz, $CDCl_3$): 148.66, 148.58, 148.43, 147.30, 143.13, 142.88, 125.55, 125.45, 124.88, 124.78, 123.70, 123.57, 120.30, 120.16, 111.03, 109.33, 108.83, 99.16, 98.99, 98.80, 98.60, 98.25, 82.59, 82.42, 82.05, 81.90, 81.81, 81.72, 81.48, 81.07, 80.24, 79.67, 79.15, 78.91, 71.48, 71.25, 70.83, 70.59, 70.10, 63.25, 61.70, 61.39, 61.31, 61.27, 61.23, 59.07, 59.03, 58.89, 58.78, 58.62, 58.58, 58.54, 58.35, 58.31, 58.26, 58.21, 56.23, 55.99, 51.19.HR-MS (MALDI-TOF): *m/z* calcd for ($C_{252}H_{375}N_9O_{114}Na$),5377.3817, found: 5377.3805.

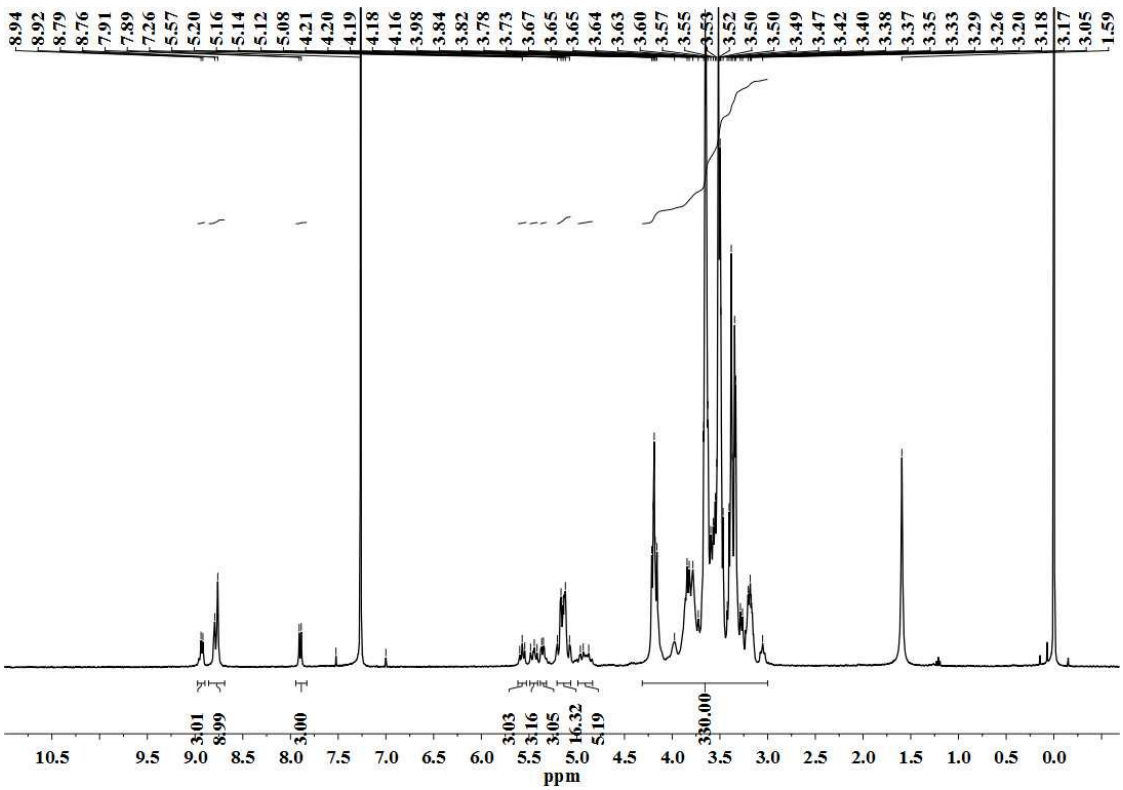


Figure S1. ^{1}H NMR (400 MHz) spectrum of CHBC-1 in $CDCl_3$ at room temperature.

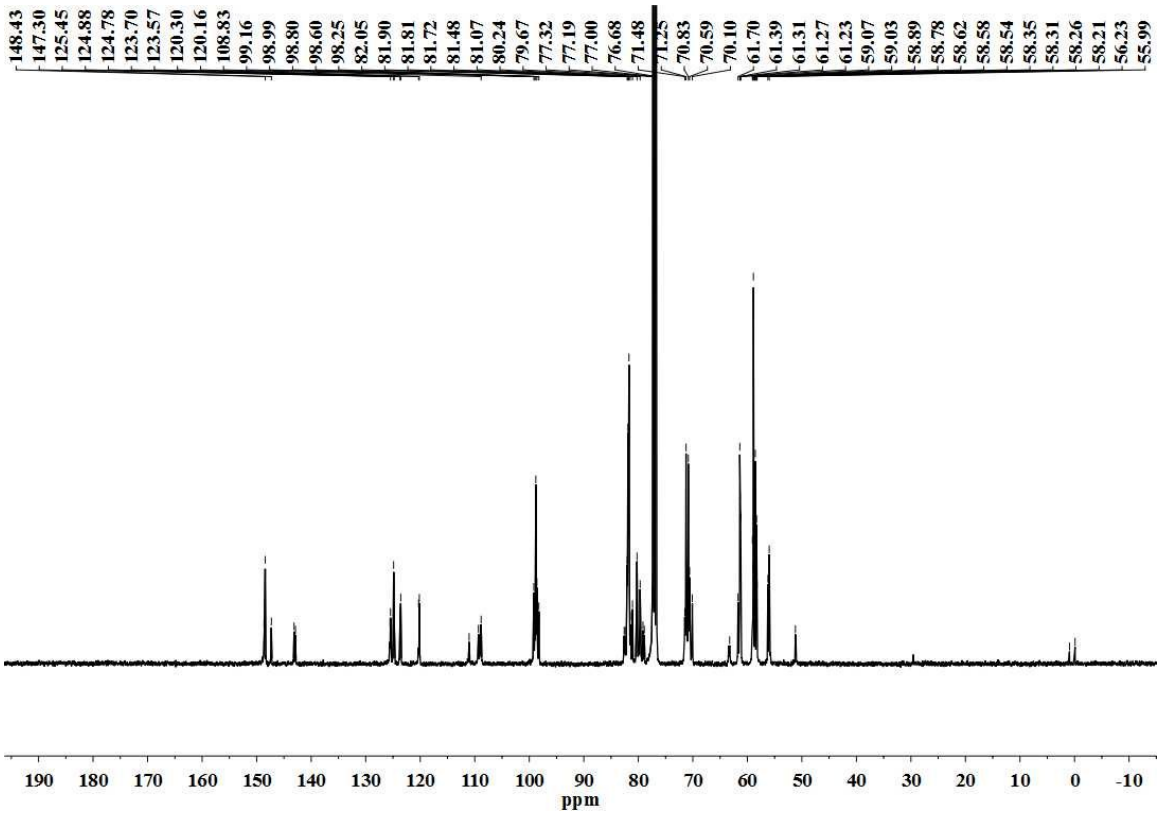
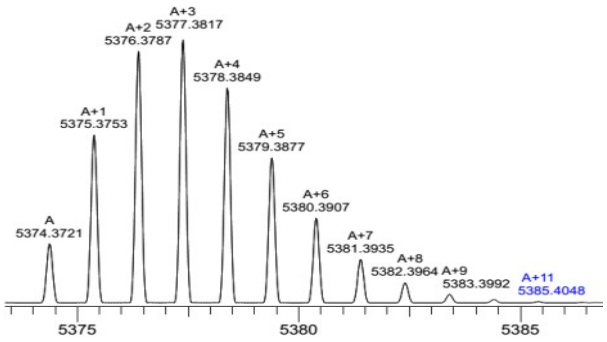


Figure S2. ^{13}C NMR (100 MHz) spectrum of CHBC-1 in $CDCl_3$ at room temperature.

Calcd.



Exp.

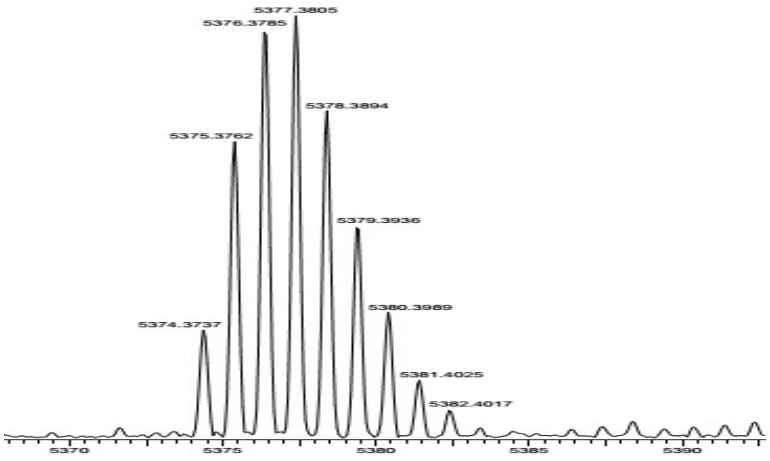


Figure S3. MALDI-MS spectrum of CHBC-1.

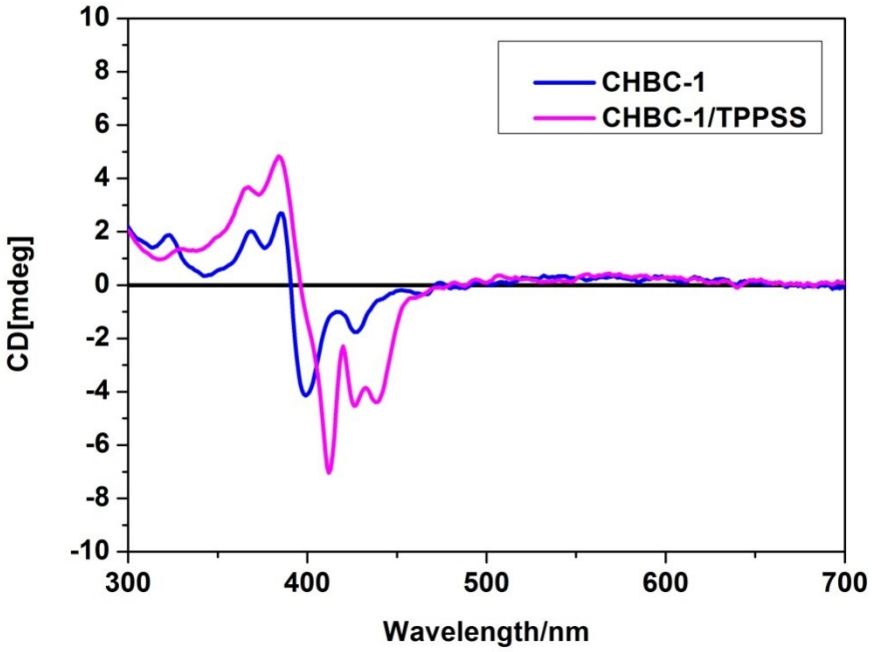


Figure S4. Circular dichroism spectra of CHBC-1and CHBC-1/TPPSS in pH 7.2 phosphate buffer ([CHBC-1] = 5×10^{-6} M, [TPPSS] = 7.5×10^{-6} M).

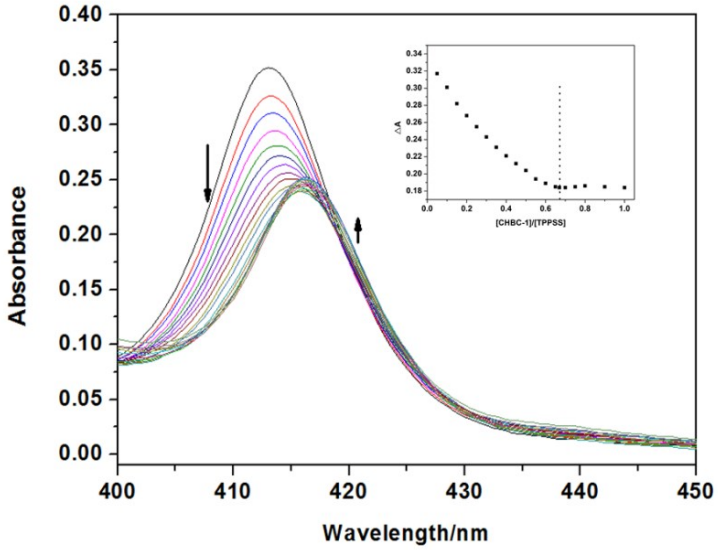


Figure S5. Soret band spectral changes of TPPSS (1.0×10^{-6} M) upon addition of 0–1.0 equivalents of CHBC-1 in phosphate buffer (pH 7.2, 0.1 M) solution at 25 °C. Inset: the absorption change versus CHBC-1/TPPSS molar ratio recorded at λ=412 nm.

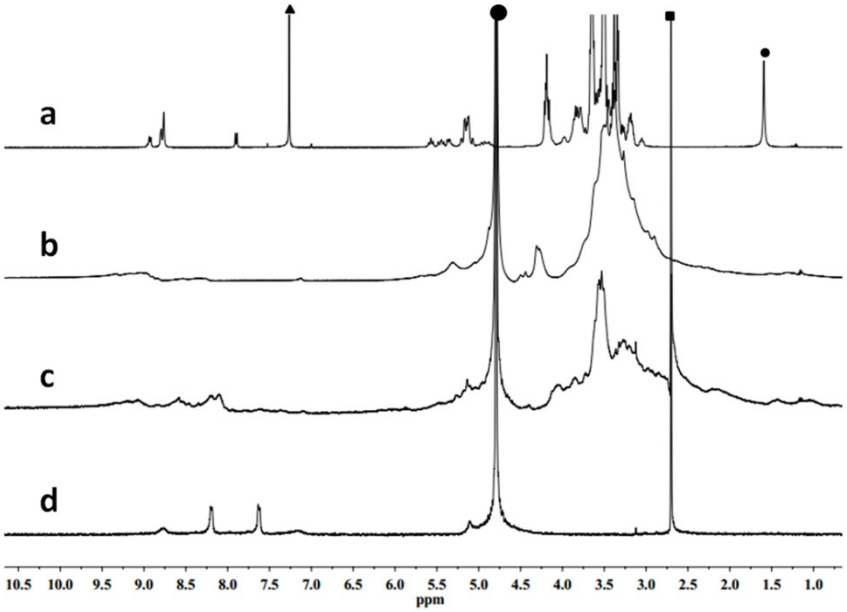


Figure S6. ^{1}H NMR spectra of CHBC-1 in (a) $CDCl_3$, (b) D_2O, (c) CHBC-1/TPPSS complex in D_2O, and (d) TPPSS in D_2O, respectively.

Figure S7. 2D NOESY spectrum of CHBC-1 in $CDCl_3$.

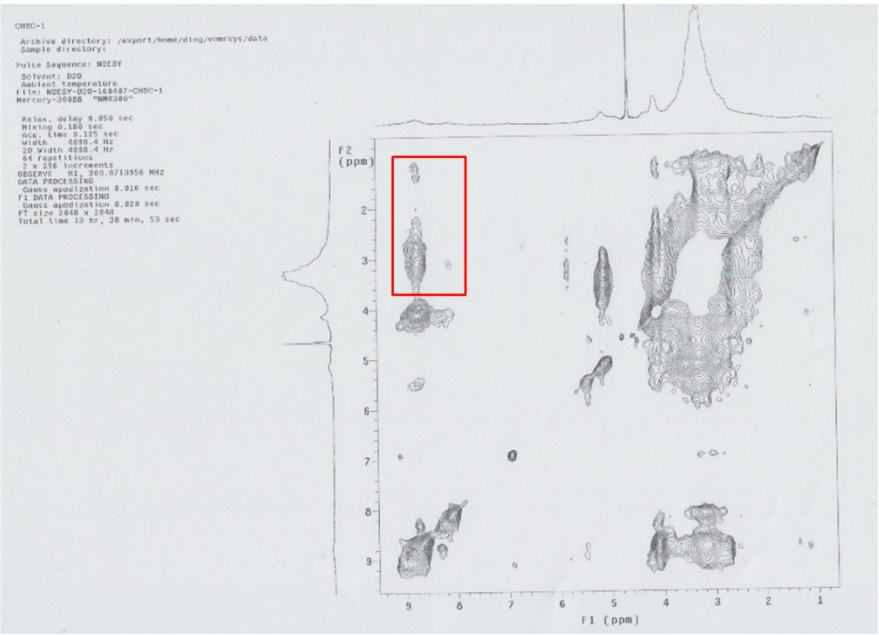
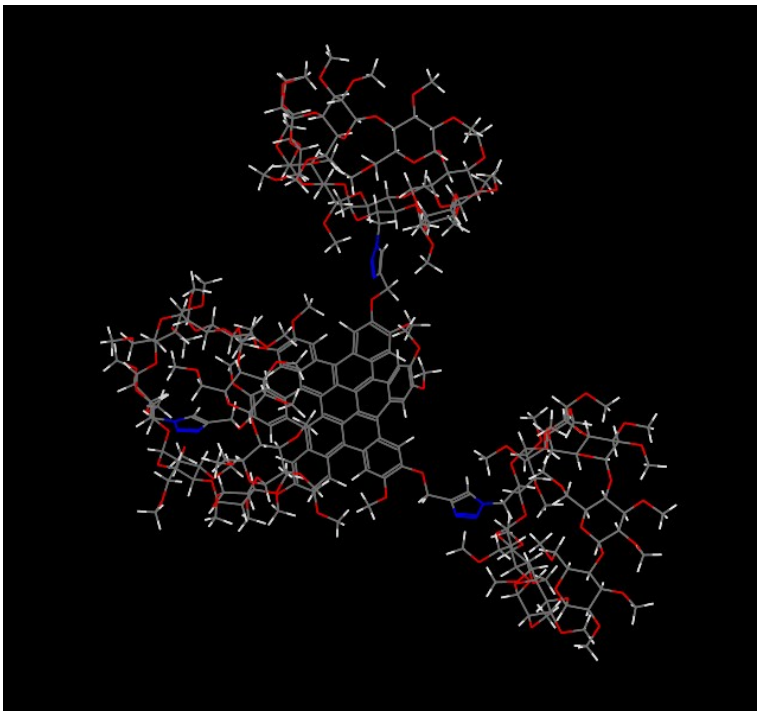
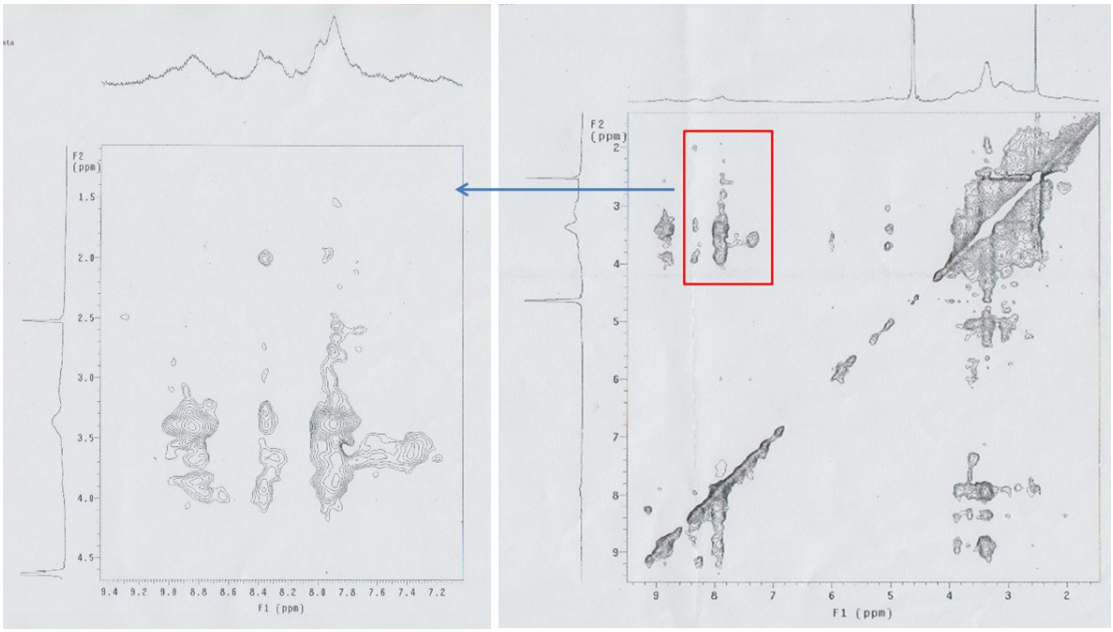


Figure S8. 2D NOESY spectrum of CHBC-1 in D_2O.



FigureS9. Molecular energy minimization structure through molecular modulation of CHBC-1.



FigureS10. 2D NOESY spectrum of CHBC-1/TPPSS=2/3 in D_2O.

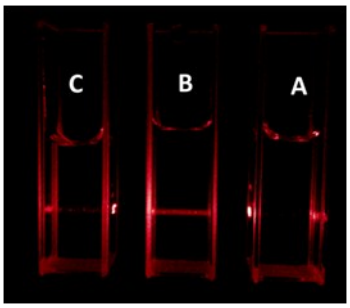


Figure S11. Picture: the Tyndall effect of CHBC-1/TPPSS(A: CHBC-1, B: CHBC-1/TPPSS, C: TPPSS).

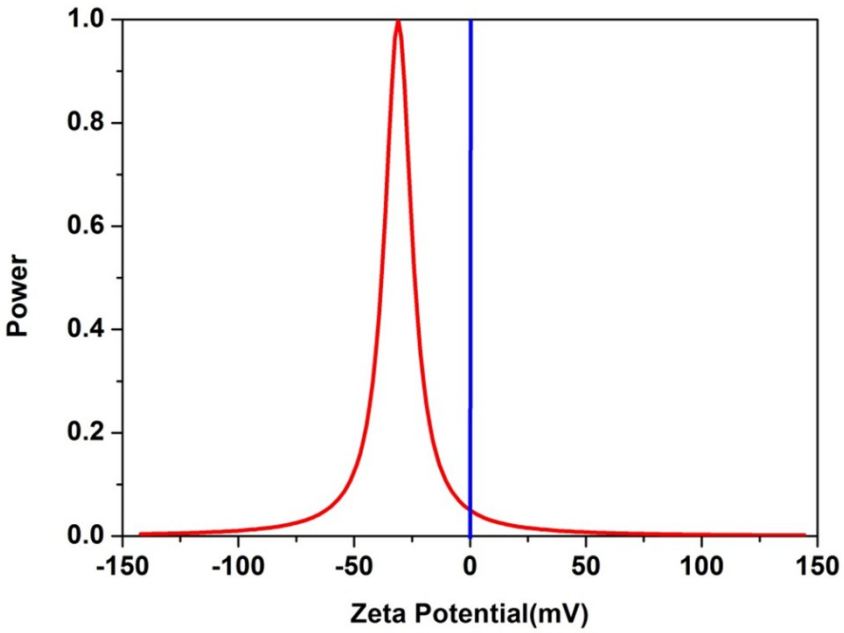


Figure S12. Zeta potential of CHBC-1/TPPSS: -31.06 mV.

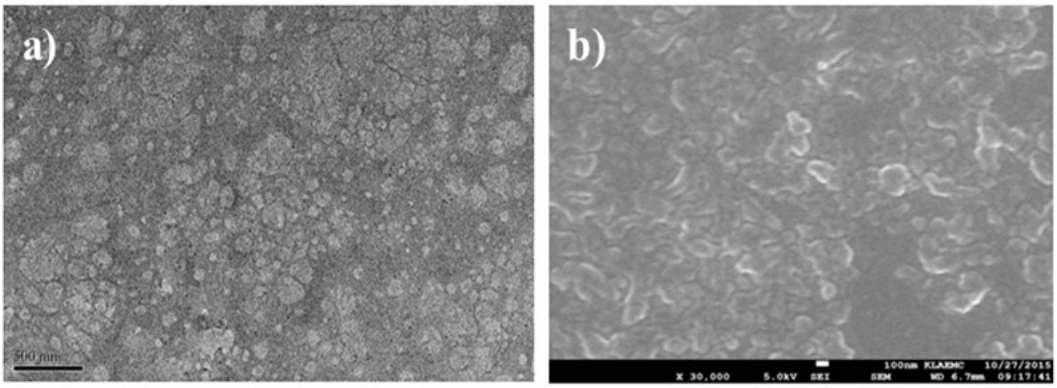


Figure S13. TEM image of CHBC-1/TPPSS (a); SEM images of CHBC-1/TPPSS (b).

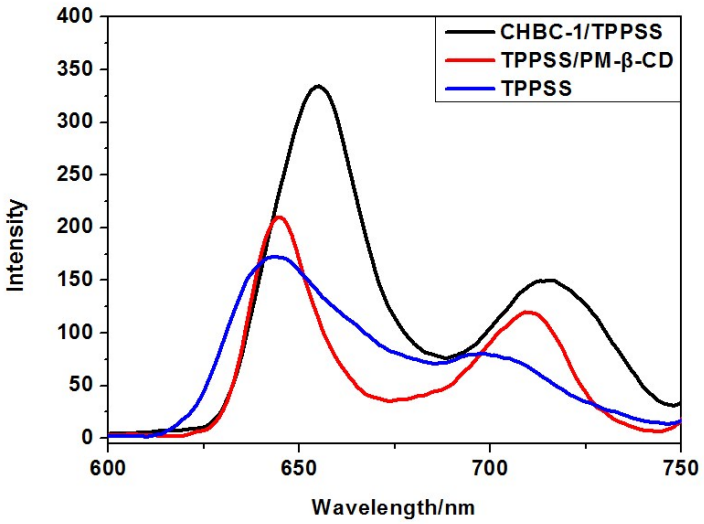


Figure S14. Fluorescence spectral of TPPSS, TPPSS/PM-β-CD and CHBC-1/TPPSS systems in pH 7.2 phosphate buffer solution at 25 °C ([CHBC-1] = 1×10^{-6} M, [TPPSS] = 1.5×10^{-6} M, [PM-β-CD] = 3×10^{-6} M, λ_{ex}= 380 nm).

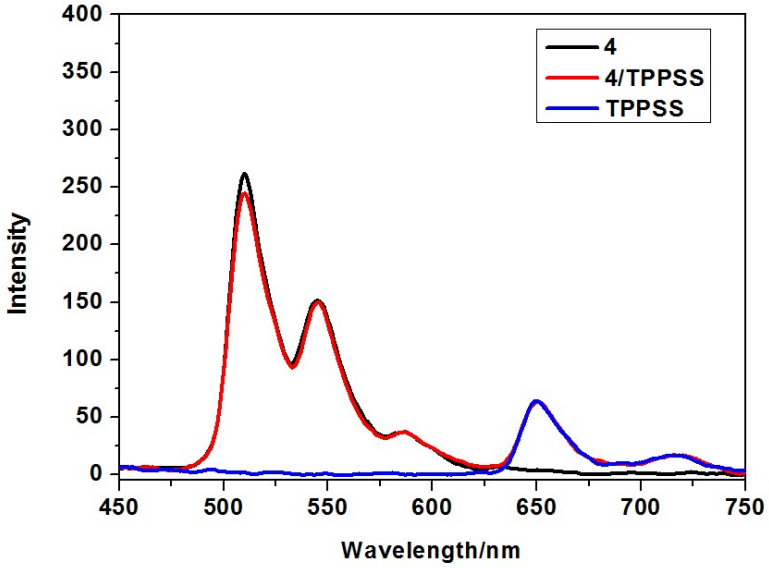


Figure S15. Fluorescence spectral of **4**, **4**/TPPSS and TPPSS in DMSO at 25 °C ([**4**] = 1×10^{-6} M, [TPPSS] = 1.5×10^{-6} M, λ_{ex} = 380 nm).

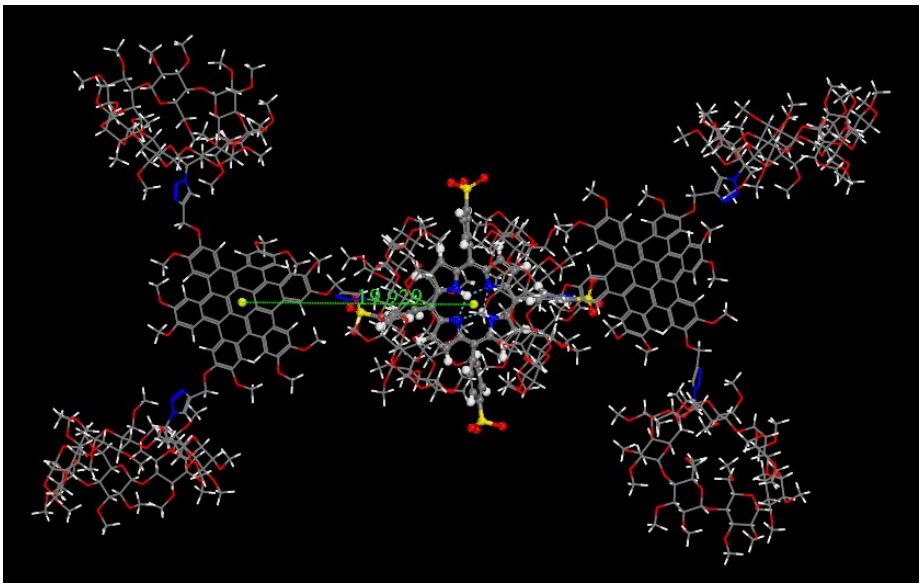


Figure S16. Molecular energy minimization structure through molecular modulation of CHBC-1/TPPSS with the measured center distance between CHBC-1/TPPSS. (In order to calculate the center-to-center distance between CHBC-1 and TPPSS, two imaginary atoms were set at the center of CHBC-1 and TPPSS.)

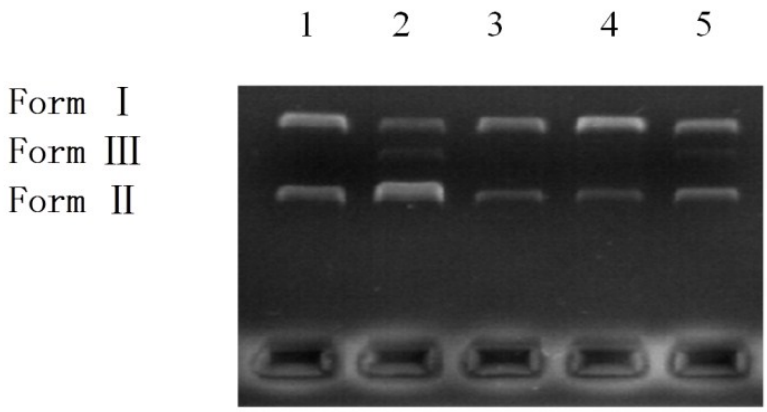


Figure S17. Gel electrophoresis diagram showing the cleavage of pBR322 DNA (5 ng/μL) by adding CHBC-1/TPPSS and different scavengers in the presence of visible light.

Lane 1: blank control.

Lane 2: CHBC-1/TPPSS (0.01 mM/0.015 mM)

Lane 3: CHBC-1/TPPSS/KI (0.01 mM/0.015 mM/25 mM)

Lane 4: CHBC-1/TPPSS/NaN_3 (0.01 mM/0.015 mM/80 mM)

Lane 5: CHBC1/TPPSS/DMSO (0.01 mM/0.015 mM/0.3 μL) in the presence of visible light.

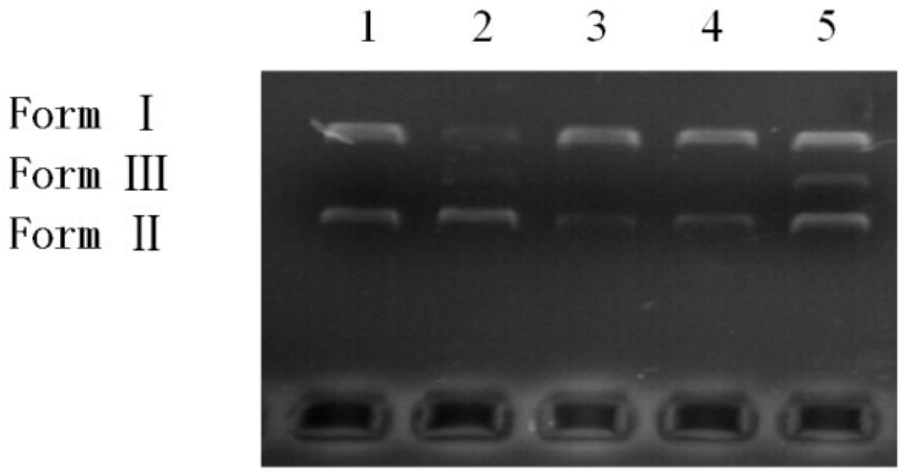


Figure S18. Agarose gel showing cleavage of pBR322DNA (5 ng/μL) by adding CHBC-1 and different scavengers in the presence of visible light.

Lane 1: blank control.

Lane2: CHBC-1 (0.01 mM)

Lane 3: CHBC-1/KI (0.01 mM/25 mM)

Lane 4: CHBC-1/NaN_3 (0.01 mM/80 mM)

Lane 5: CHBC-1/DMSO (0.01 mM/0.3 μL) in the presence of visible light.

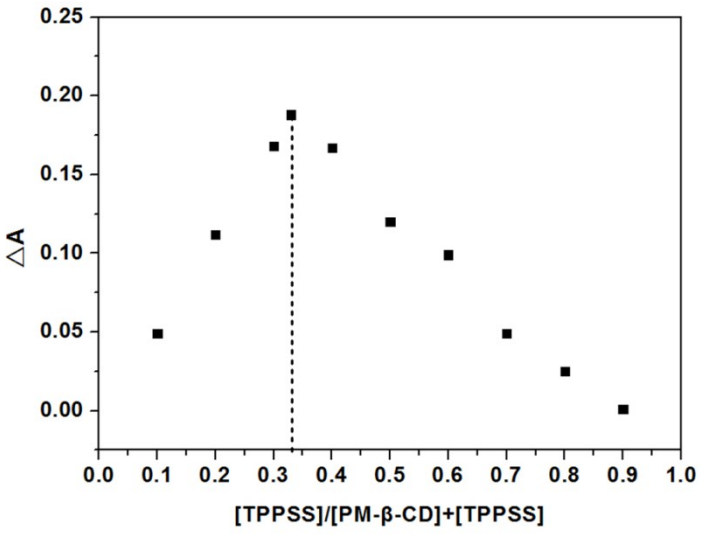
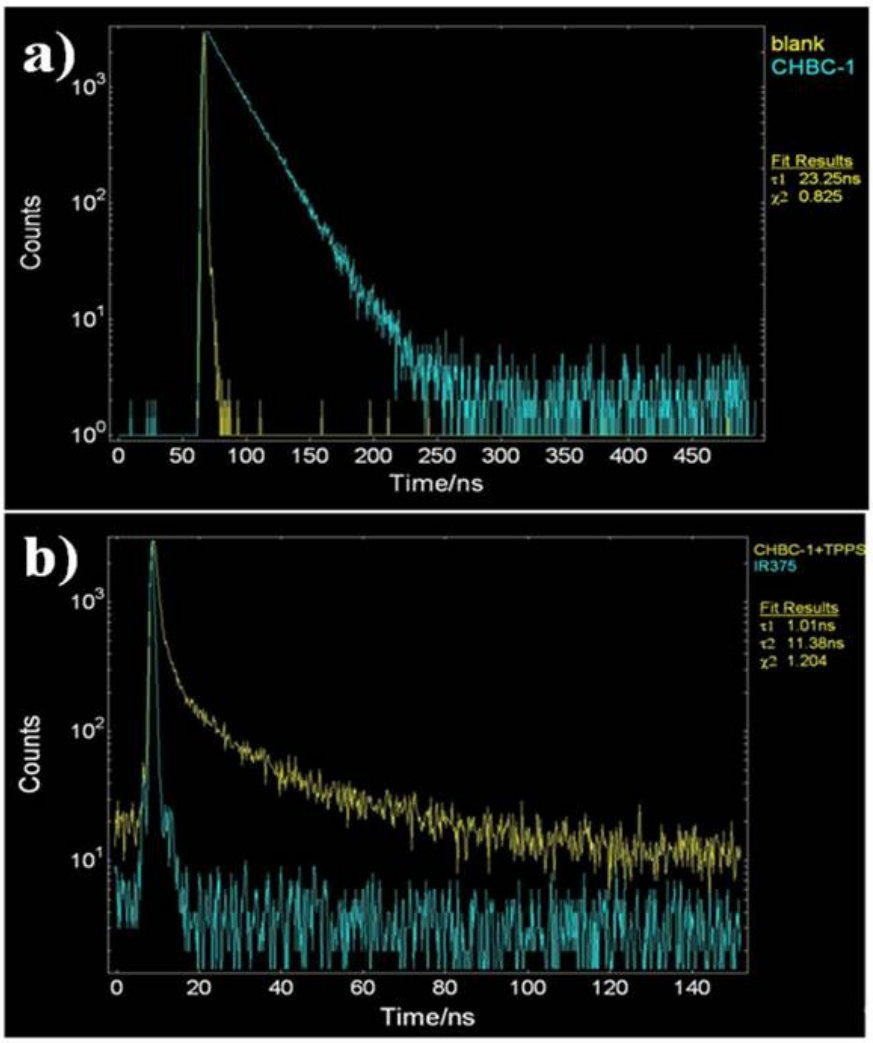


Figure S19. Job plot for TPPSS upon complexation with PMCD in pH 7.2 phosphate buffer (absorption changes recorded at 410 nm for TPPSS; [PMCD] + [TPPSS] = 5 × 10^{-6} M).



sample	Lifetime(ns)(%contribution)		
	τ_1	τ_2	τ
CHBC-1	23.25		23.25
CHBC-1/TPPSS	1.01(74.12%)	11.38(25.88%)	3.69

Figure S20. Fluorescence lifetimes of CHBC-1 (a) and CHBC-1/TPSS (b) in pH 7.2 phosphate buffer solution at 25 °C ([CHBC-1] = 1×10^{-5} M, [TPPSS] = 1.5×10^{-5} M, λ_{ex} = 375 nm).

References:

1. (a) A. Kamal, S. Prabhakar, M. J. Ramaiah, P. V. Reddy, C. R. Reddy, A. Mallareddy, N. Shankaraiah, T. L. N. Reddy, S. Pushpavalli and M. Pal-Bhadra, *Eur. J. Med. Chem.*, 2011, **46**, 3820-3831; (b)S. Kotha and K. Mandal, *Eur. J. Org. Chem.*, 2006, 5387-5393; (c) J. Yu, Y. Chen, Y.-H. Zhang, X. Xu and Y. Liu, *Org. Lett.*, 2016, **18**, 4542-4545; (d) Q. Zhang, H. Peng, G. Zhang, Q. Lu, J. Chang, Y. Dong, X. Shi and J. Wei, *J. Am. Chem. Soc.*, 2014, **136**, 5057-5064.