

**Electronic Supplementary Information for**

**Novel supramolecular assemblies of repulsive DNA-anionic porphyrin complexes based on covalently modified multi-walled carbon nanotubes and cyclodextrins**

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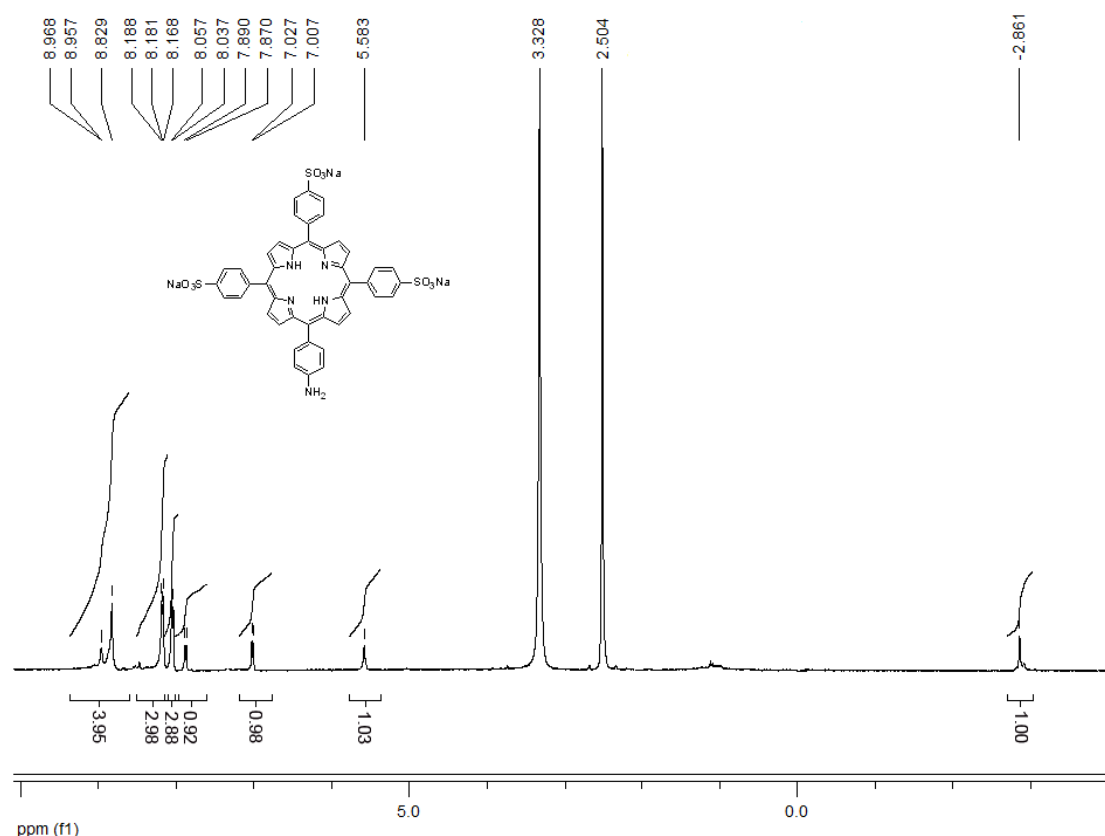
**Figure S1**,  $^1\text{H}$  NMR spectrum of **1** in  $\text{DMSO-}d_6$ ;

**Figure S2**, FT-IR spectra of **1**, **2** and **2-non**;

**Figure S3**, thermogravimetric curve of **2**.

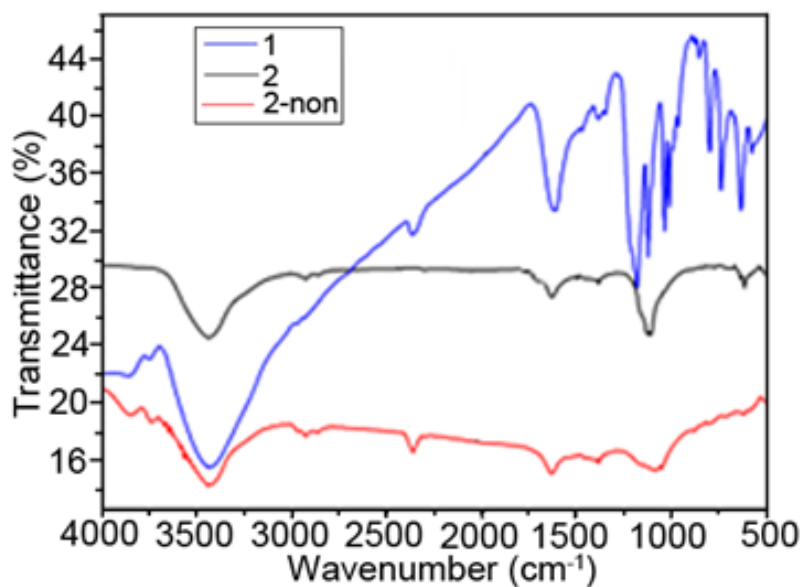
**Figure S4**, the fluorescence spectra of **2-non** interacting with (A)  $\alpha$ -CD (B)  $\beta$ -CD and then with DNA (left inset, dotted lines) .

**Figure S5**, the fluorescence spectra of **1** interacting with (A)  $\alpha$ -CD (B)  $\beta$ -CD and then with DNA (left inset, dotted lines).



**Figure S1.**  $^1\text{H}$  NMR spectrum of **1** in  $\text{DMSO-}d_6$  as the trisodium salt

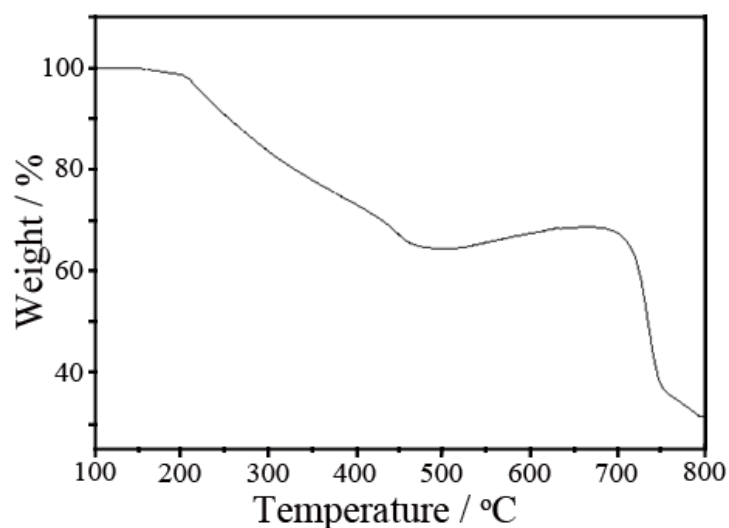
$\delta$  8.97 (broad, 8 H,  $\beta$ -pyrrole), 8.19 (d, 6 H, 4-sulfonatophenyl), 8.06 (d, 6 H, 4-sulfonatophenyl), 7.89 (d, 2 H, 4-aminophenyl), 7.03 (d, 2 H, 4-aminophenyl), 5.58 (s, 2 H, amino  $\text{NH}_2$ ), -2.86 (s, 2 H, pyrrole NH).



**Figure S2.** FT-IR spectra of **1**, **2** and **2-non**

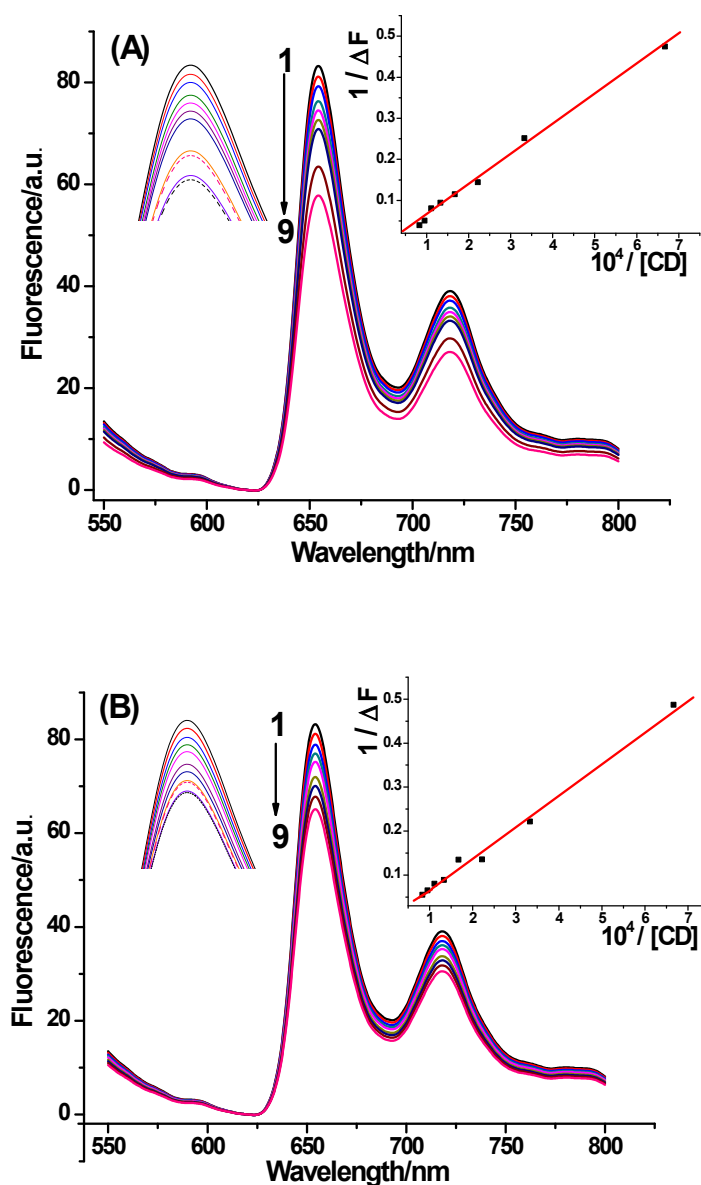
The FT-IR spectrum of ATSP/MWCNTs **2** shows characteristic vibrations centered at 1642 and 1050  $\text{cm}^{-1}$ , which should be respectively attributed to the carbonyl group (C=O) and the C-N single bond, supporting the formation of the vital amide bond between ATSP and MWCNTs.

In the spectrum of **2-non**, the small shoulder peak on the left side of 1642  $\text{cm}^{-1}$  (another characteristic absorption for the C=O bond) could not be observed, which indicated that there wasn't a carbonyl group in **2-non** and **1** was absorbed onto MWCNTs surface in a non-covalent way.

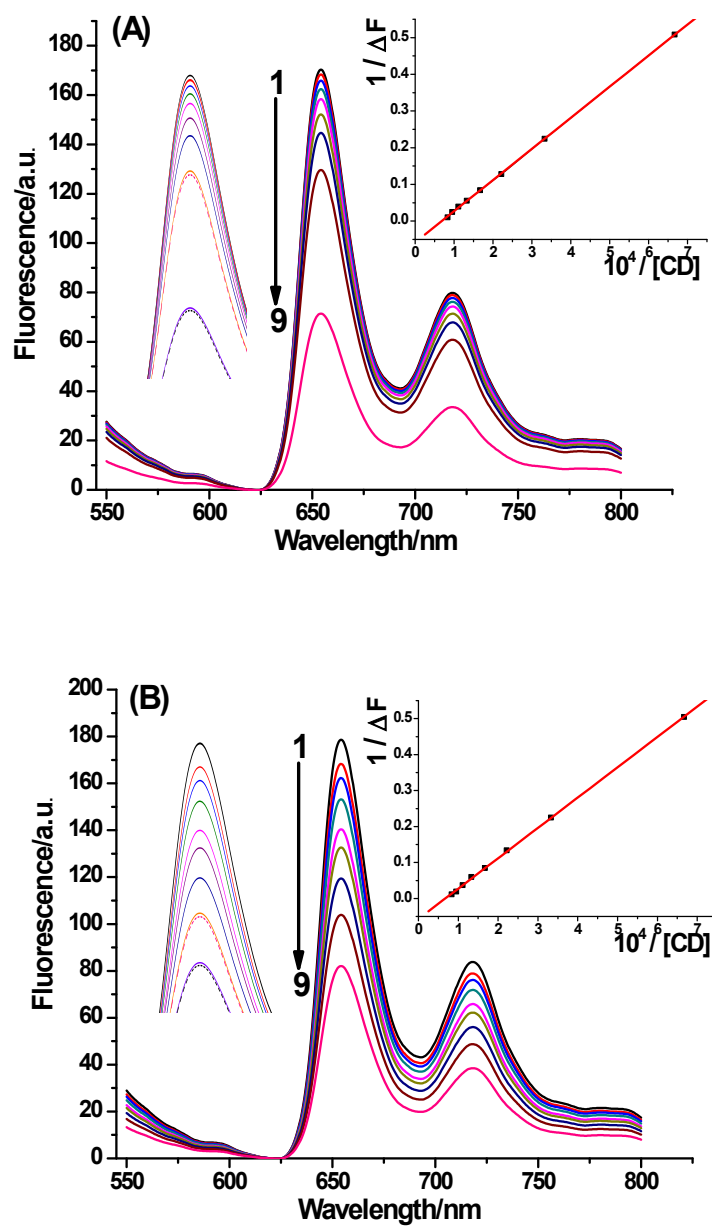


**Figure S3.** The thermogravimetric curve of **2**

The TGA curve of **2** showed a continuous weight loss starting from 200 to 800  $^{\circ}\text{C}$ , with a major weight loss at 720  $^{\circ}\text{C}$ . The decompositions in the temperature ranges from 200 to 480  $^{\circ}\text{C}$  and 720 to 800  $^{\circ}\text{C}$  were assigned to the attached porphyrin and the MWCNTs, respectively.



**Figure S4.** The fluorescence spectra of **2-non** ( $9 \times 10^{-3}$  g L $^{-1}$ ) in the pH 7.04 phosphate buffer solution containing various concentration of (A)  $\alpha$ -CD (B)  $\beta$ -CD at 25 °C (excitation wavelength 423 nm). The concentration of CD is: (1) 0 M; (2)  $1.5 \times 10^{-5}$  M; (3)  $3.0 \times 10^{-5}$  M; (4)  $4.5 \times 10^{-5}$  M; (5)  $6.0 \times 10^{-5}$  M; (6)  $7.5 \times 10^{-5}$  M; (7)  $9.0 \times 10^{-5}$  M; (8)  $1.05 \times 10^{-4}$  M; (9)  $1.2 \times 10^{-4}$  M. Right inset: the linear plot of  $1/(F-F_0)$  versus  $1/[CD]$ . Left inset: the contrast fluorescence spectra of the following addition of 72  $\mu$ L of DNA ( $1.44 \times 10^{-5}$  M) in (A)  $\alpha$ -CD (B)  $\beta$ -CD with a concentration of (8)  $1.05 \times 10^{-4}$  M; (9)  $1.2 \times 10^{-4}$  M (the dotted lines for DNA).



**Figure S5.** The fluorescence spectra of ATSP 1 ( $1.2 \times 10^{-6}$  M) in the pH 7.04 phosphate buffer solution containing various concentration of (A)  $\alpha$ -CD (B)  $\beta$ -CD at 25 °C (excitation wavelength 423 nm). The concentration of CD is: (1) 0 M; (2)  $1.5 \times 10^{-5}$  M; (3)  $3.0 \times 10^{-5}$  M; (4)  $4.5 \times 10^{-5}$  M; (5)  $6.0 \times 10^{-5}$  M; (6)  $7.5 \times 10^{-5}$  M; (7)  $9.0 \times 10^{-5}$  M; (8)  $1.05 \times 10^{-4}$  M; (9)  $1.2 \times 10^{-4}$  M. Right inset: the linear plot of  $1/(F-F_0)$  versus  $1/[DNA]$ . Left inset: the contrast fluorescence spectra of the following addition of 72  $\mu$ L of DNA ( $1.44 \times 10^{-5}$  M) in (A)  $\alpha$ -CD (B)  $\beta$ -CD with a concentration of (8)  $1.05 \times 10^{-4}$  M; (9)  $1.2 \times 10^{-4}$  M (the dotted lines for DNA).