Electronic Supplementary Information

for

Supramolecular self-assembly and photophysical properties of pillar[5]arene-stabilized CdTe quantum dots mediated by viologens

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Contents

1. Materials and Methods

All solvents used in this study were reagent grade and purchased from commercial sources. Deionized H_2O was used in all experiments unless otherwise noted. Transmission electron microscopy (TEM) images were collected on a Hitachi H-800 instrument, where the accelerating voltage was 200 kV. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 80V spectrometer. Zeta potential measurements were tested on a Zetasizer Nano 9300 instrument. UV-*vis* spectroscopy and fluorescence spectroscopy were performed on a Shimadzu UV-2550 spectrophotometer and a Shimadzu RF-5301PC spectrophotometer, respectively. NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer. CP[5]A, MV and bridged bis(MV)s were synthesized according to our previous report[S1].

2. Preparation of MPA@QDs and CP[5]A@QDs

2.1 Synthesis of CdTe QDs stabilized with MPA

MPA-stabilized CdTe QDs was synthesized according to the literature report[S2]. The solutions of $CdCl_2$ and NaHTe precursor were refluxed under N_2 protection to give CdTe QDs. In a typical experiment, $CdCl_2$ (35 mg) and 3-mercaptopropionic acid (MPA, 39 mg) were added into deionized H_2O (150 mL). Then, the pH of the mixture was adjusted to 9 using sodium hydroxide solution (1 M). N_2 was bubbled through the reaction mixture for about 30 min. Subsequently, the NaHTe solution (0.33 M) was rapid injected into the mixture, and the ratio of Cd^{2+}/MPA/Te^{2-} was 1/2.4/0.2. Then, the mixture was hearted to 90 °C under a N_2 atmosphere. After 4 h, CdTe QDs were obtained, showing orange fluorescent emission under UV-light irradiation. The obtained CdTe QDs were further purified by precipitation-redispersion cycle to remove the excess of MPA. Finally, the precipitate of CdTe QDs (MPA@QDs) was dispersed into deionized H_2O for further experiment.

2.2 Sonochemical preparation of carboxylatopillar[5]arene-stabilized CdTe QDs (CP[5]A@QDs)

CP[5]A@QDs were prepared *via* a sonochemical method. An aqueous solution of CP[5]A (50 mg) was added into a purified CdTe solution (10 mL), and the pH of the resulting mixture was adjusted to 14 with NaOH solution (1 M). Then, the mixture was placed in a high-intensity ultrasound bath (150 W, 40 KHz) for about 60 min. Then, Me_2CO (5 mL) was poured into the reaction mixture. Subsequently, excess of unreacted CP[5]As were removed by centrifugation and washing of the crude product with Me_2CO to give pure CP[5]A@QDs, which were further dispersed in deionized H_2O (30 mL) for future experiments.

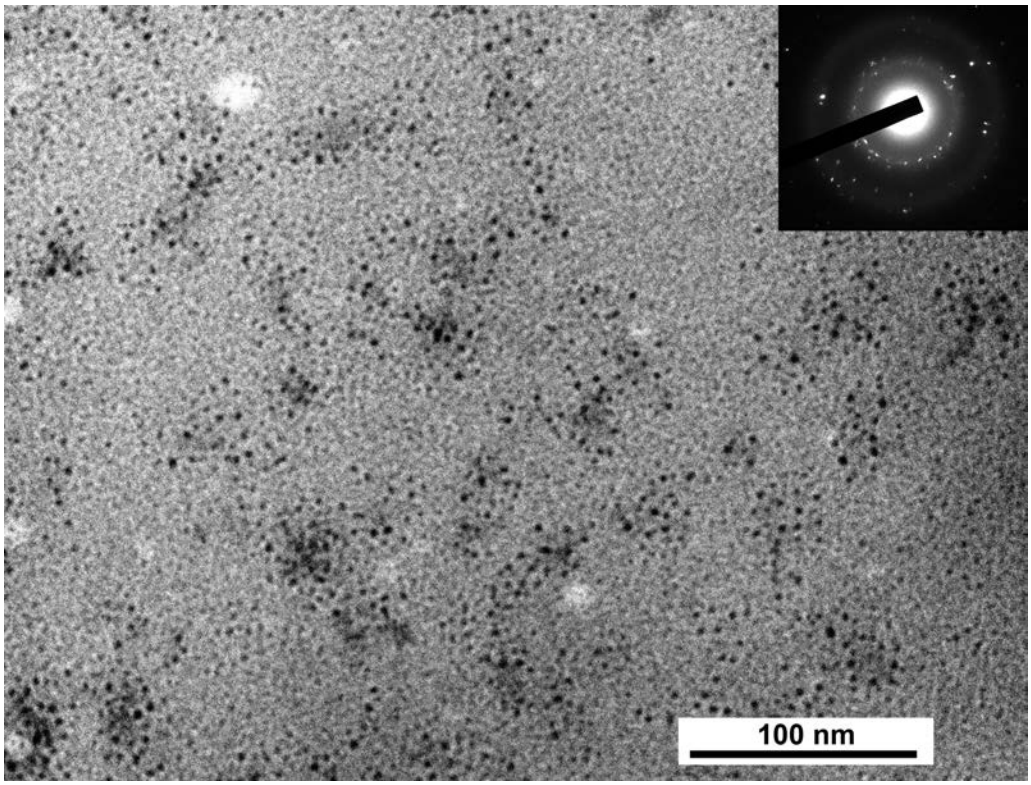

Figure S1. TEM image and selected area electron diffraction (SAED) pattern of CP[5]A@QDs.

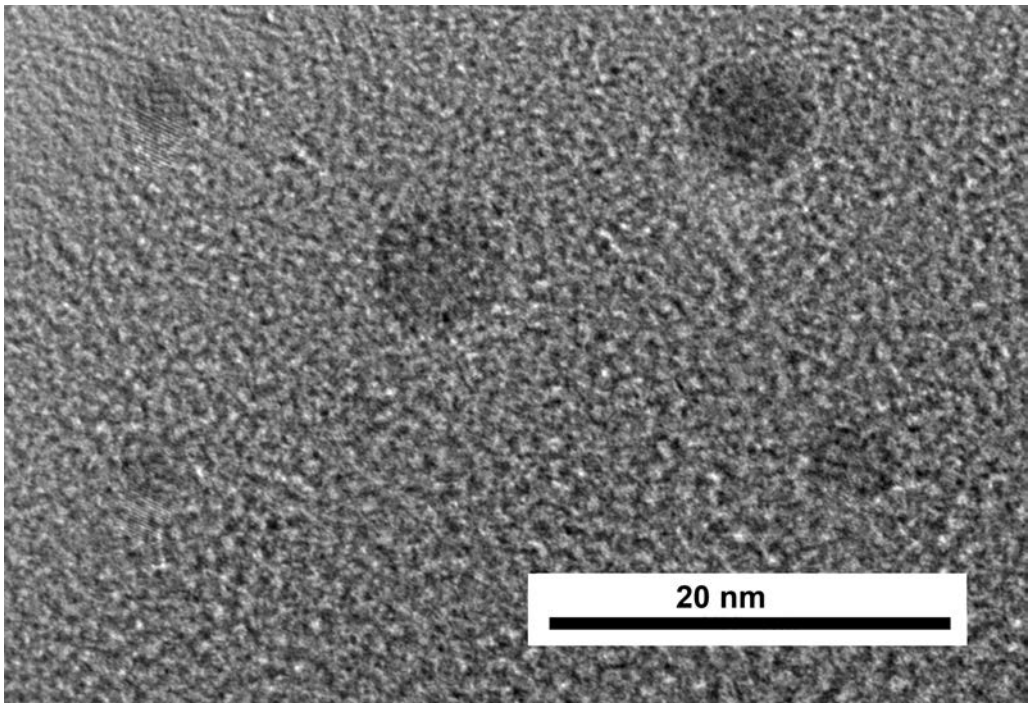

Figure S2. HR-TEM image of CP[5]A@QDs.

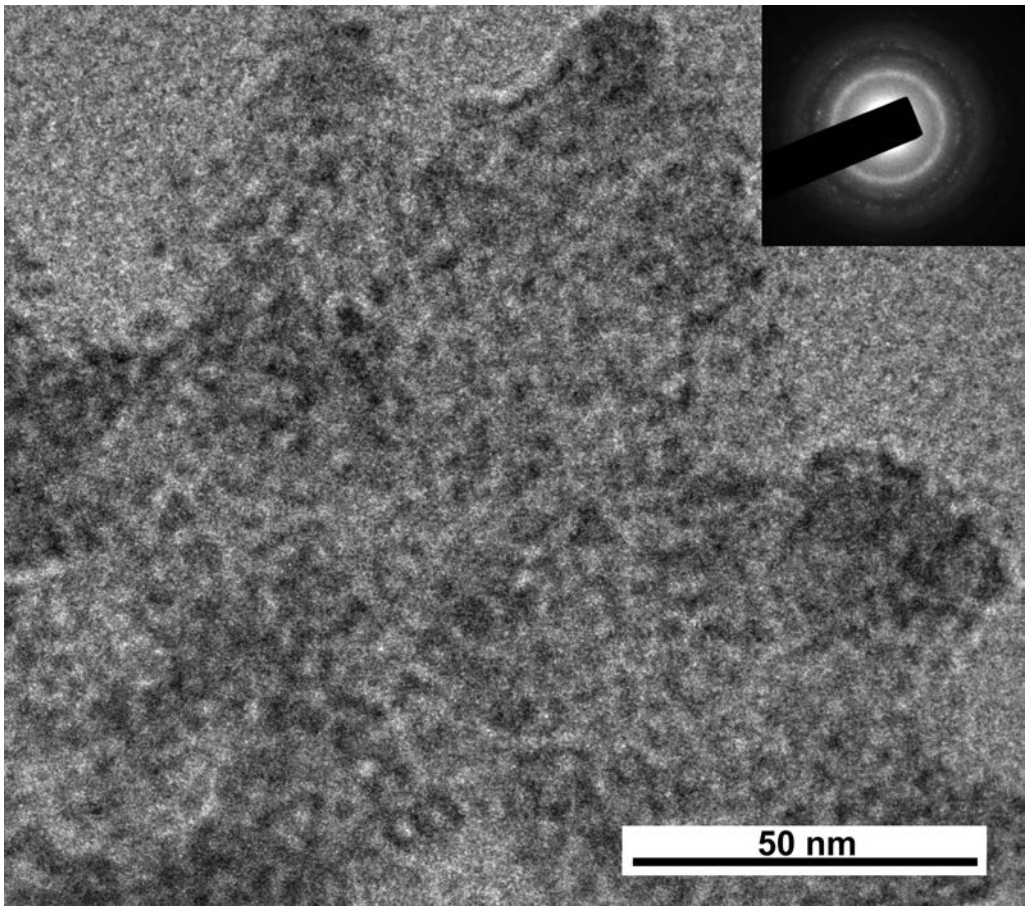

Figure S3. TEM image and selected area electron diffraction (SAED) pattern of CP[5]A@QD oligomer.

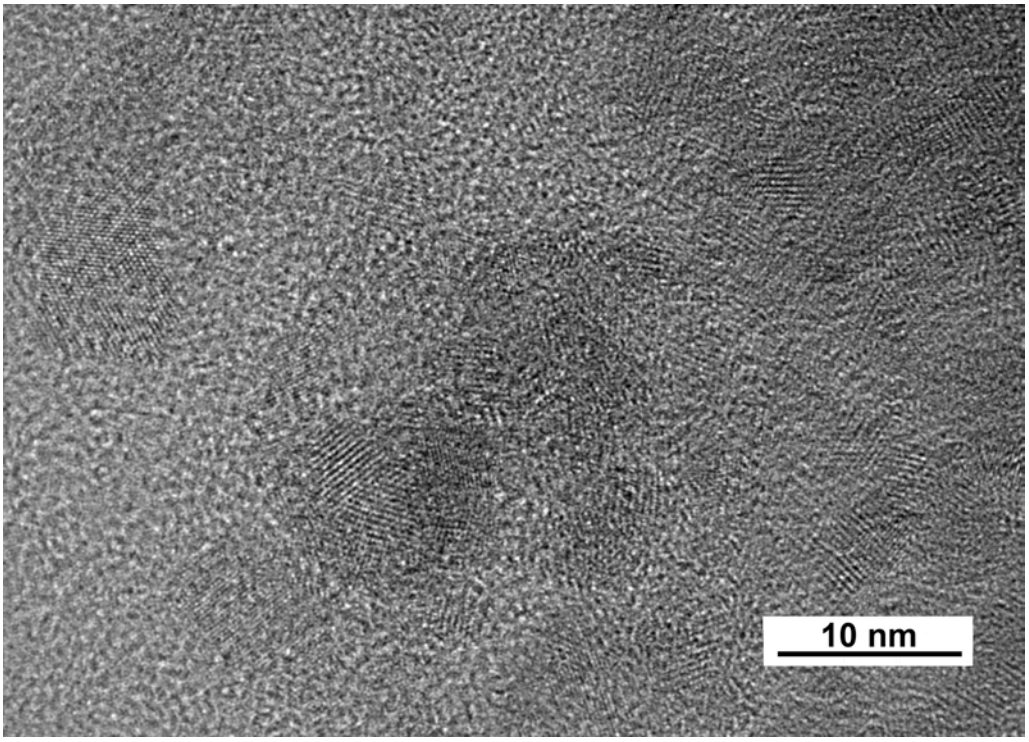

Figure S4. HR-TEM image of CP[5]A@QDs oligomer.

3 The Influence of Viologen III on the Zeta Potentials of MPA@QDs and CP[5]A@QD

Table S1. Zeta potentials of MPA@QDs and CP[5]A@QDs before and after the addition of bridged bis(MV)s solution (1.0×10^{-5} M).

QDs	Amount of Bridged Bis(MV)s Solution Added	Zeta potential (mV)
MPA@QDs	0 μL	-40.7
MPA@QDs	2 μL	-21.0
MPA@QDs	6 μL	-3.8
CP[5]A@QDs	0 μL	-52.6
CP[5]A@QDs	2 μL	-55.1
CP[5]A@QDs	6 μL	-55.5
CP[5]A@QDs	10 μL	-55.9
CP[5]A@QDs	14 μL	-56.6
CP[5]A@QDs	20 μL	-56.8
CP[5]A@QDs	25 μL	-63.3
CP[5]A@QDs	35 μL	-61.2
CP[5]A@QDs	45 μL	-58.4

4 Visualization of CP[5]A@QD Solutions in Different Conditions

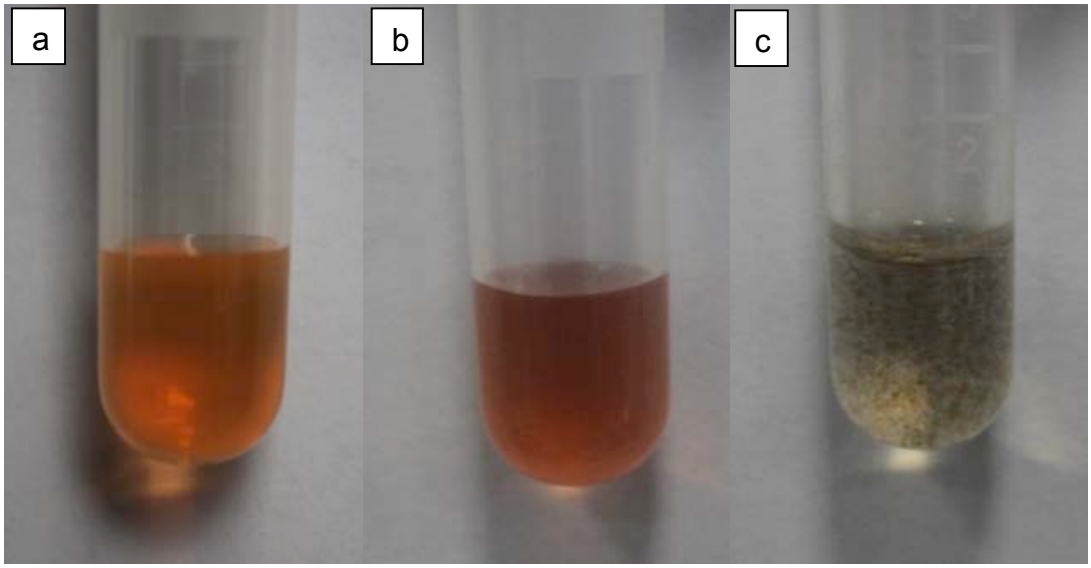

Figure S5. Aqueous solutions of (a) CP[5]A@QDs; (b) CP[5]A@QDs upon the addition of a small amount of bridged bis(MV)s; (c) CP[5]A@QDs upon the addition of excess of bridged bis(MV)s.

5 The ^{1}H NMR Spectra of Host-Guest Interaction of CP[5]A and Viologens[S3,S4]

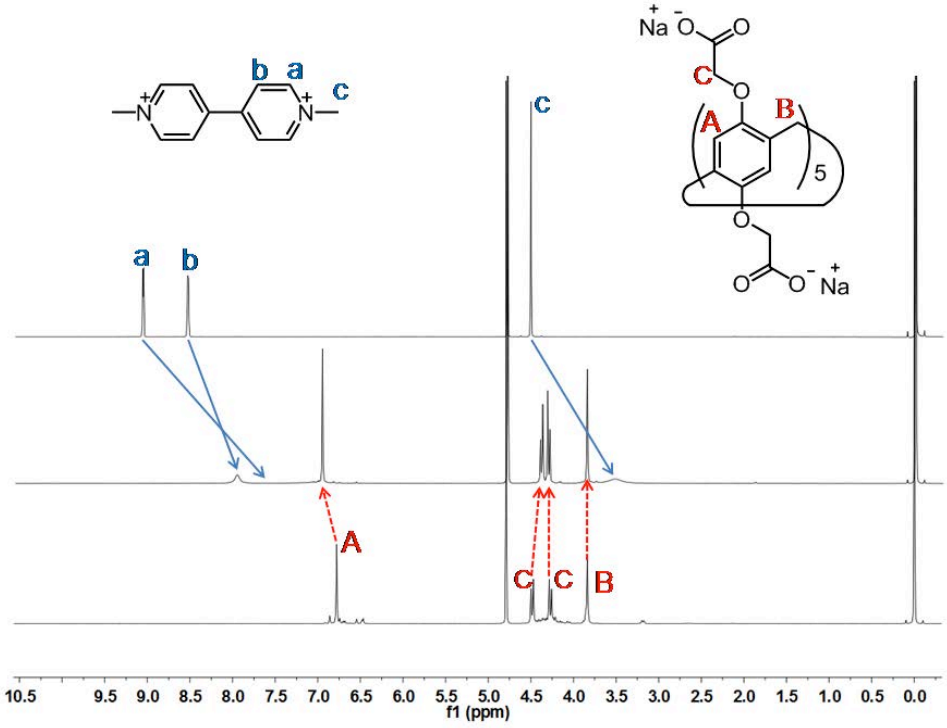

Figure S6. ^{1}H NMR spectra of host-guest interaction of CP[5]A and MV.

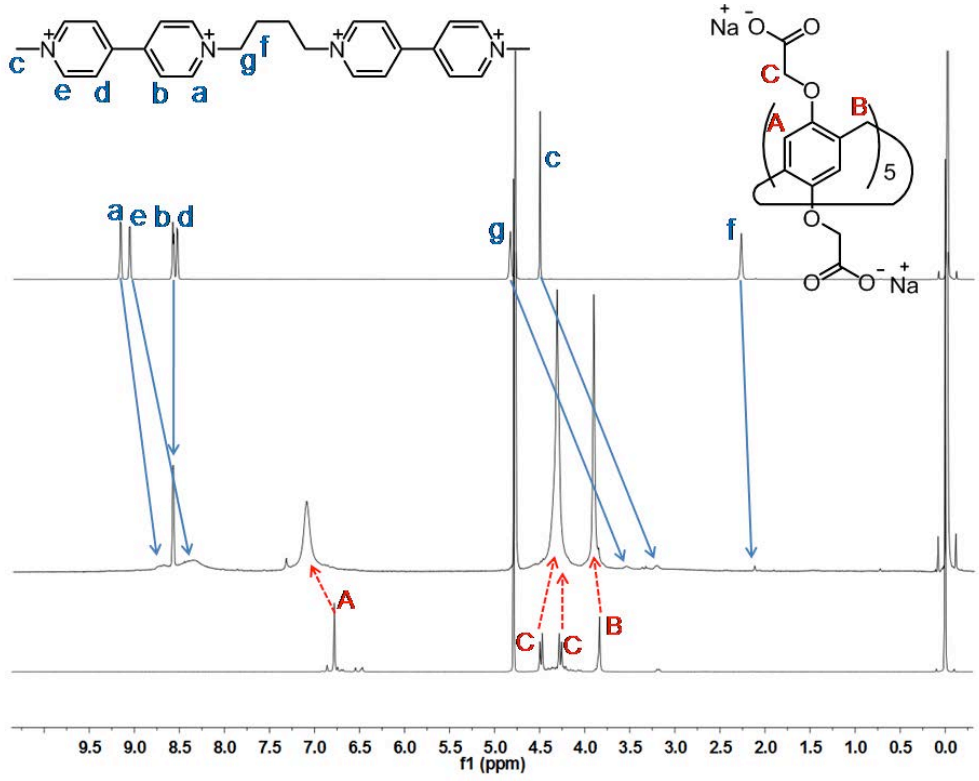

Figure S7. ^{1}H NMR spectra of host-guest interaction of CP[5]A and bridged bis(MV)s.

References

S1. H. Li, D.-X. Chen, Y.-L. Sun, Y. B. Zheng, L.-L. Tan, P. S. Weiss and Y.-W. Yang, *J. Am. Chem. Soc.* 2013, **135**, 1570–1576.

S2. H. Zhang, D. Wang, B. Yang and H. Möhwald, *J. Am. Chem. Soc.*, 2006, **128**, 10171–10180.

S3. T. Ogoshi, M. Hashizume, T.-a. Yamagishi and Y. Nakamoto, *Chem. Commun.*, 2010, **46**, 3708–3710.

S4. C. Li, Q. Xu, J. Li, F. Yao and X. Jia, *Org. Biomol. Chem.*, 2010, **8**, 1568–1576.