Supporting information

Redox Responsive Supramolecular Amphiphiles Based on Reversible Charge Transfer Interactions

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1. Materials and experiments

Synthesis of PYR and MV: PYR was synthesized according to our previous work. [1] 1,1'-dimethyl-4,4'-bipyridine-1,1'-diium iodide (MV): 4-4'-bipyridine and excessive CH_3I were dissolved in CH_3CN and the mixture was kept stirring refluxing for one night. After evaporation of CH_3CN, the solid was washed with diethyl ether for three times to give a red product. (Yield: 78%) ^{1}H-NMR spectra were recorded on a JOEL JNM—ECA300 apparatus (300 MHz, DMSO, 25 ℃, TMS): δ =9.01 (d, 4H), δ =8.74 (d, 4H), δ =2.46 (s, 6H).

***Assembly preparation*: Typically, PYR-MV complex was prepared by mixing PYR and MV, in a molar ratio of 1:1, in THF, a good solvent for forming charge transfer complex. THF was then removed under reduced pressure. The dissolution–evaporation procedure was repeated several times, to yield a yellow solid. The solid was finally dissolved in water into an aqueous solution with a concentration of 1.0×10^{-4} M.

UV/vis spectra and fluorescence emission spectra: UV-vis spectra were obtained using a HITACHI U-3010 spectrophotometer. Fluorescence spectra were obtained using a HITACHI F-7000 apparatus at slit 5.0 and at a scanning rate of 240 nm/min. The excitation wavelength was 339 nm.

Electrochemical Measurements: CV measurement was carried out using a potentiostat (Autolab PGSTAT12, The Netherlands) in a conventional three-electrode glass electrochemical cell at ambient temperature by taking Ag/AgCl (saturated KCl) electrode as reference electrode. The working electrode was using a bare Au electrode. The solutions for the electrochemical measurements were purged prior to the measurements by continuously bubbling highly purified nitrogen through them for 30 min, and a nitrogen atmosphere environment was maintained during the electrochemical measurements. The concentration of the PYR in the solution was 1.0×10^{-4} M. The scanning rate was 0.10 V/s.

ESEM experiments: ESEM images were captured using a FEI Quanta 200 FEG apparatus. The aqueous solution was dripped directly onto a copper bowl and then inserted into the chamber for observation. Inside the chamber, the temperature was set to be 0℃ and the gas pressure was 500 pa.

TEM experiments: The samples were prepared by drop-coating the aqueous solution on the carbon coated copper grid and then negatively stained with Phosphotungstic acid solution. TEM observation was performed on a JEMO 2010 Electron microscopy operating at an acceleration voltage of 110 kV.

Fluorescence microscopy: A drop of aqueous solution was dripped onto a colorless piece of glass and was directly under observation. Fluorescence microscopy images were recorded on a DMI6000 B apparatus.

AFM experiments: A freshly prepared mica sheet was immersed into the aqueous solution for 20 min. After that, the mica sheet was taken out of the solution and was dried under room temperature. After that, the mica sheet was observed using a Nanoscope Ⅳ.

2. Absorption spectra and fluorescence emission of the complexes compared with PYR itself.

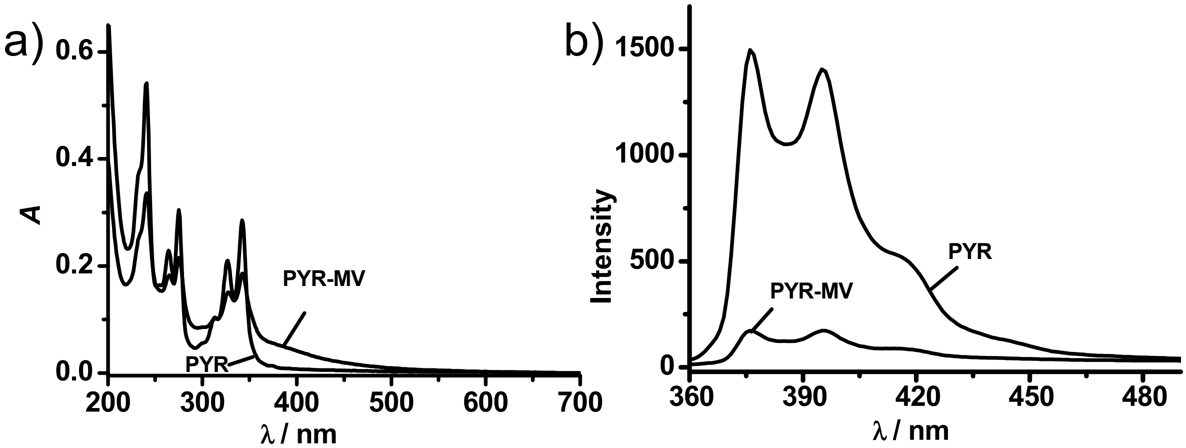

Fig. S1 a) UV/Vis absorption and b) fluorescence emission of PYR and PYR-MV spectrum complex.

5 The solvent is water and the concentration of PYR unit is 1.0×10^{-4} M.

3. Absorption spectra and fluorescence emission of the complexes with different PYR/MV molar ratios.

A series of PYR–MV complexes with different donor/acceptor ratios were prepared. As the MV-content increased, the emission intensity decreased, without any change in the spectral pattern, indicating that the quenching process occurred by charge transfer from the pyrenyl units to the viologen units. The concentration of PYR is 1.0×10^{-4} M.

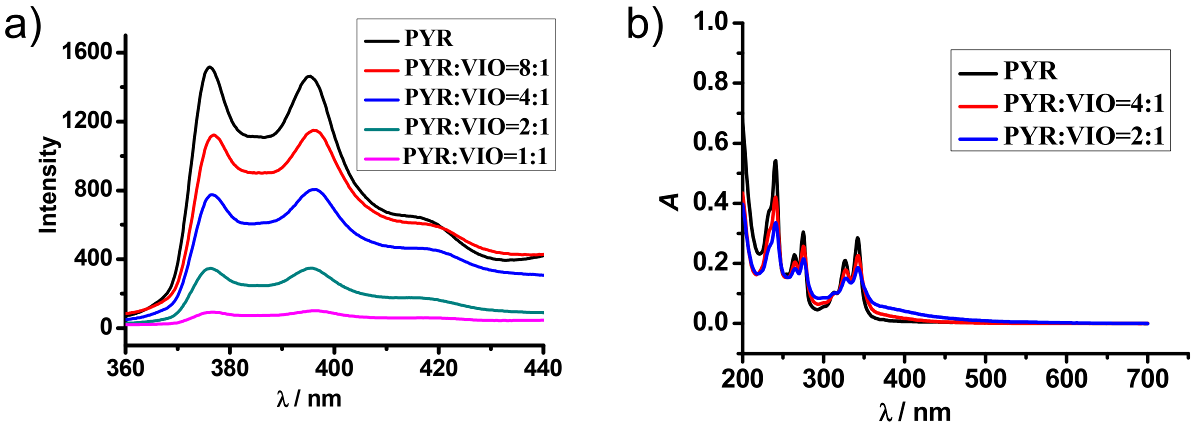

Fig. S2: UV/Vis absorption spectrum a) and fluorescence emission b) of the complexes with different PYR/MV molar ratios. The solvent is water and the concentration of PYR unit is 1.0×10^{-4} M.

4. AFM and DLS results of PYR-MV aggregates after reduction

The self-assembly behaviors of PYR-MV complex after reduction were also studied by AFM and DLS tests. The size and the structures are consistent with the TEM and ESEM results. The concentration of PYR and PYR-MV are both 1×10^{-4} M.

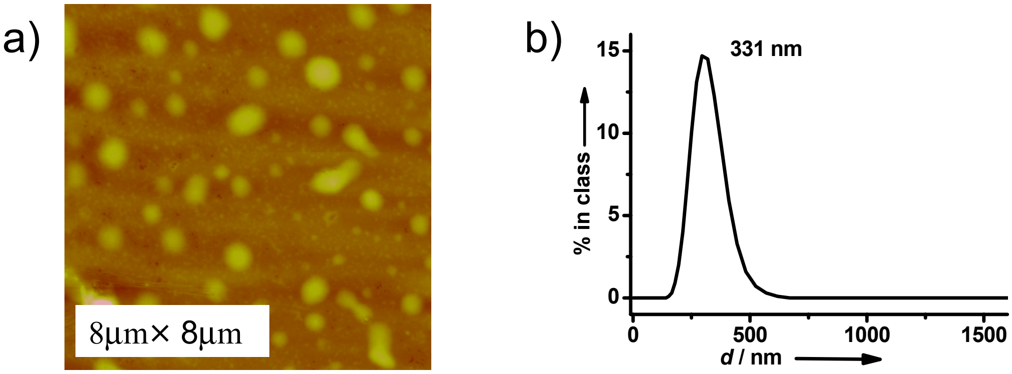

Fig. S3: a) AFM observation and b) DLS result of the PYR-MV aggregates after reduction.

5. TEM results of PYR-MV after one cycle of redox and reduction.

When the radical state of the PYR-MV complex was further oxidized with H_2O_2, the irregular aggregates reformed (Figure S4a). On further reduction, the vesicular structure appeared again (Figure S4b).

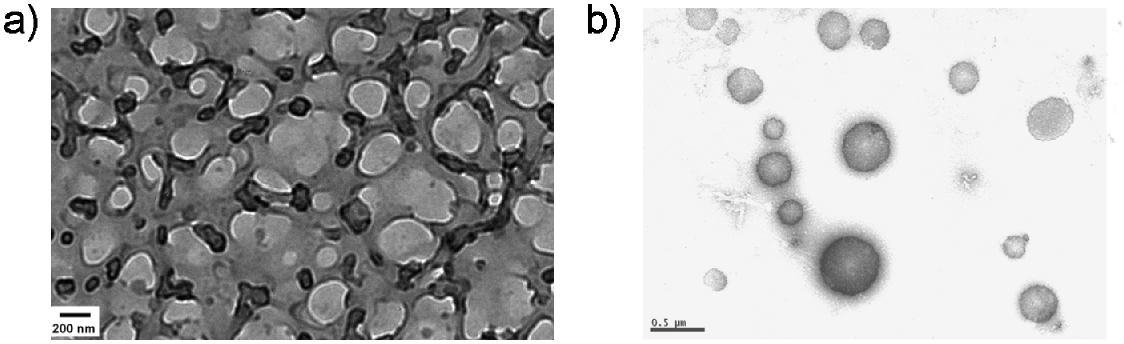

Fig. S4: TEM results of a) PYR-MV after reduction and subsequent oxidation and b) PYR-MV after redox and again reduction

5. The process of morphology changes from vesicles to irregular continuous aggregates.

The process of the vesicle-irregular aggregates transformation was monitored by ESEM. As shown in Figure S5, gradual vesicle fusion was observed.

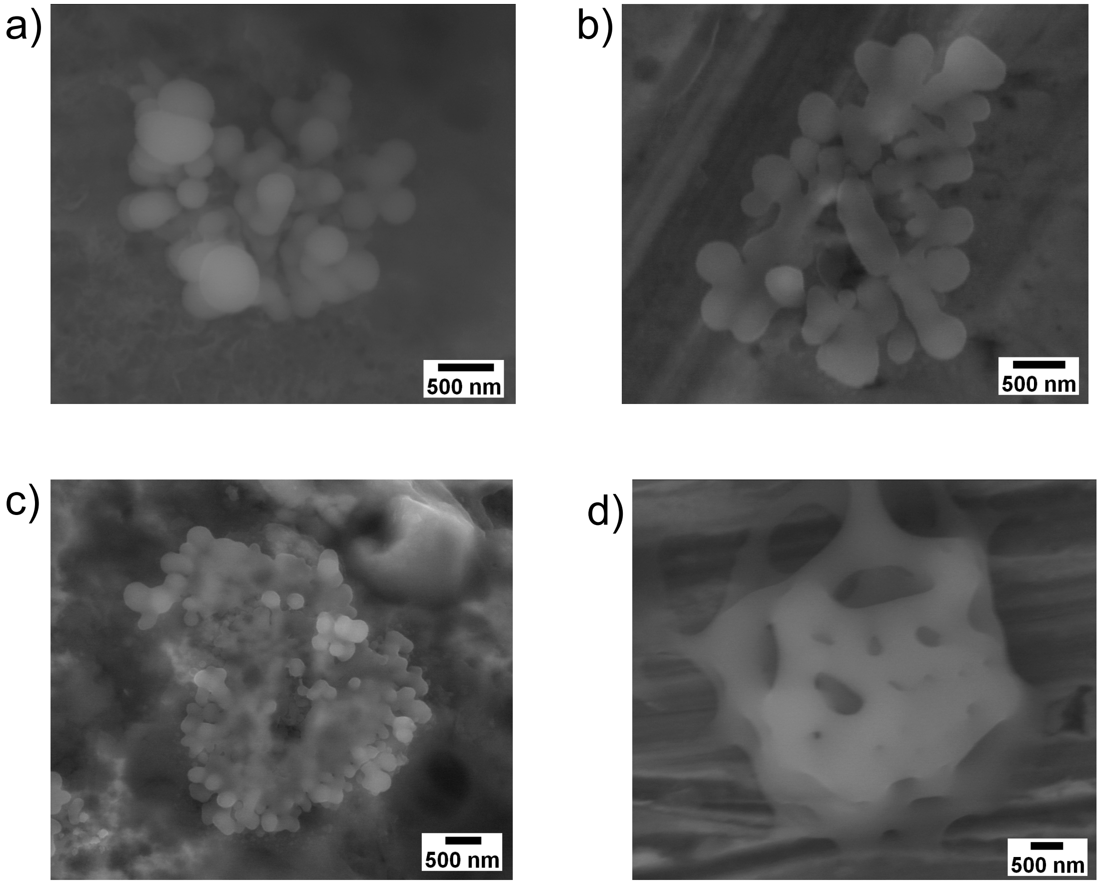

Fig. S5: ESEM images of the vesicles upon oxidation after a) 5 min b) 10 min c) 20 min d) 30 min

6. SAXS measurements of PYR-MV during the redox process.

One drop of solution (1×10^{-4} M) was casted onto silicon surface and the solvent was evaporated at room temperature under vacuum. Then the sample was used form XRD and SAXS measurements. From the SAXS data, the Bragg peak θ is found and then the bilayer thickness d can be obtained according to the Bragg equation $d=\lambda/(2\sin\theta)$, $\lambda=0.15405$ nm.

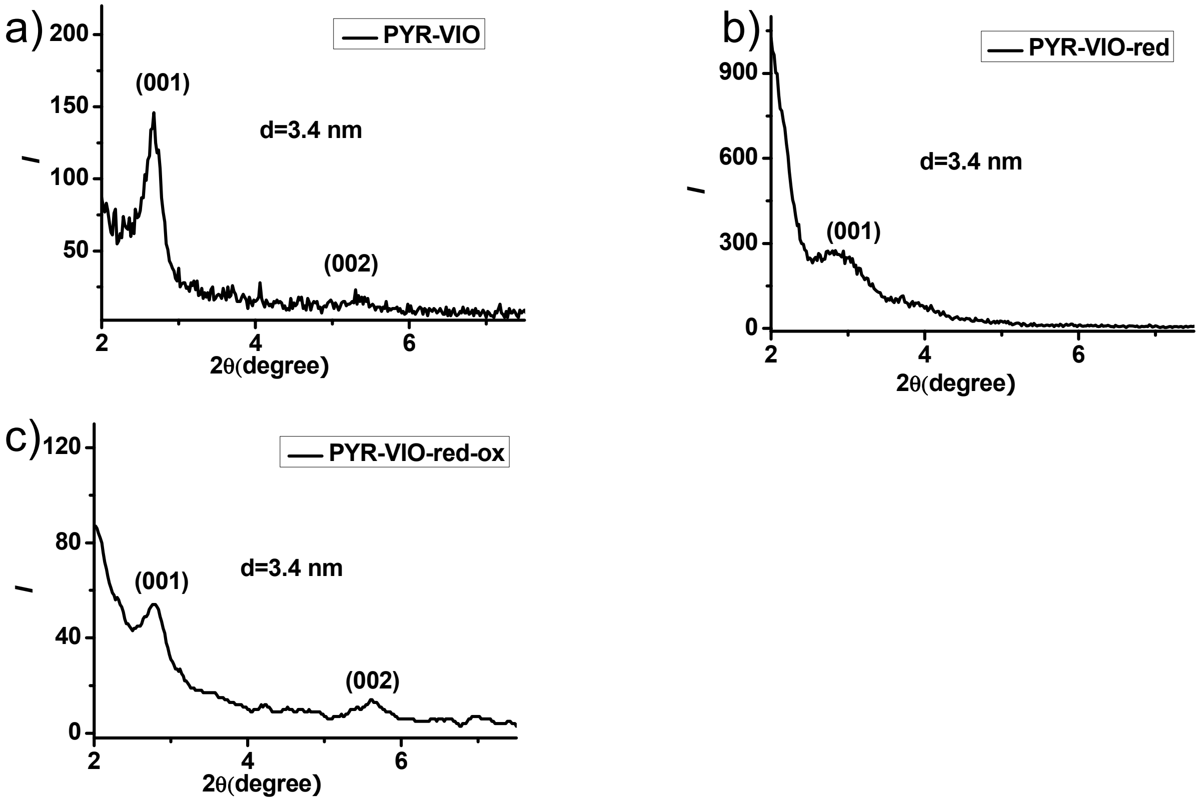

Fig. S6: SAXS results of a) PYR-MV, b) PYR-MV after reduction, c) PYR-MV after reduction and then upon oxidation.

The molecular packing was investigated using SAXS. As shown in Figure S6, during the redox process, the thickness of one single layer is the same, about 3.6 nm, indicating that the molecular framework remains unchanged. It's possibly because that when MV is at dication state, the viologen groups co-assembled with the pyrene arrays driven by CT interactions. After reduction, as a result of the relatively hydrophobic nature and the π–π interactions with pyrene of the radical MV, MV favors to stay in situ inside the hydrophobic pyrene environment of the assemblies. Therefore, the packing framework of the bilayer remains unchanged upon redox stimuli, providing good reversibility of the self-assembly structures.

Reference:

[1] C. Wang, S. C. Yin, S. L. Chen, H. P. Xu, Z. Q. Wang, X. Zhang, *Angew. Chem. Int. Ed.*, **2008**, *47*, 9049-9052.