Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

for

Fluorescent Nanoassemblies between Tetraphenylethenes and Sulfonatocalixarenes: A Systematic Study of Calixarene-Induced Aggregation

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1. Experimental Section

1.1 Materials.

All chemicals used are reagent grade unless noted. *p*-Sulfonatocalix[*n*]arenes, *n*=4, 5, 6 (SC4A, SC5A, SC6A), *p*-sulfonatocalix[4]arene tetrapropyl ether (SC4A-Pr) were synthesized and purified according to previously reported procedures.[1,2] Heparin sodium was purchased from Aladdin Industrial Corporation without further purification. Double quaternary ammonium modified tetraphenylethene (DQA-TPE) and mono quaternary ammonium modified tetraphenylethene (MQA-TPE) were synthesized and purified according to the procedures reported previously.[3] All the synthetic compounds were identified using ^{1}H NMR spectroscopy.

1.2 Fluorescence spectroscopy.

Fluorescence spectra were measure in a quartz cell (light path 10 mm) on a Varian Cary Eclipse equipped with a Varian Cary single-cell Peltier accessory to control temperature.

1.3 Dynamic light scattering (DLS) measurement.

Solution samples were examined on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (TurboCorr) at 636 nm at a scattering angle of 90°. The hydrodynamic diameter (D_h) was determined by DLS experiments at 25 °C.

2. Syntheses

2.1 Synthesis procedure.

Synthesis of 4,4',4",4"'-((ethene-1,1,2,2-tetrayltetrakis(benzene-4,1-diyl))tetrakis(oxy)) tetrakis(N,N,N-trimethylbutan-1-aminium) (TQA-TPE) (Figure S1)

936 mg (1 mmol) 1,1,2,2-tetrakis(4-(4-bromobutoxy)phenyl)ethane (TPE-Br), 7.2 g (40 mmol) 33% $N(CH_3)_3$ aqueous solution, 40 mL ethanol was added to a flask. The mixture was heated at reflux for 10 h and then cooled to room temperature. The solvent was evaporated and the residue was washed by THF, then we obtained 921 mg light yellow powder in a yield of 78.6%. ^{1}H NMR (400 MHz, D_2O, δ) (ppm): 6.97 (d, 8H), 6.70 (d, 8H), 3.97 (t, 8H), 3.29 (m, 8H), 3.02 (s, 36H), 1.86 (d, 8H), 1.73 (m, 8H).

Synthesis of 4,4',4",4"'-((ethene-1,1,2,2-tetrayltetrakis(benzene-4,1-diyl))tetrakis(oxy)) tetrakis(N,N-dimethylbutan-1-aminium) (TTA-TPE) (Figure S1)

936 mg (1 mmol) TPE-Br, 6.01 g (40 mmol) 30% $NH(CH_3)_2$ ethanol solution, 40 mL

ethanol was added to a flask. The mixture was heated at reflux for 7 h and then cooled to room temperature. The solvent was evaporated and the residue was washed by THF, then we obtained 870 mg light yellow powder in a yield of 78.0%. ^{1}H NMR (400 MHz, D_2O, δ) (ppm): 6.95 (d, 8H), 6.68 (d, 8H), 3.94 (t, 8H), 3.09 (m, 8H), 2.77 (s, 24H), 1.73 (m, 16H).

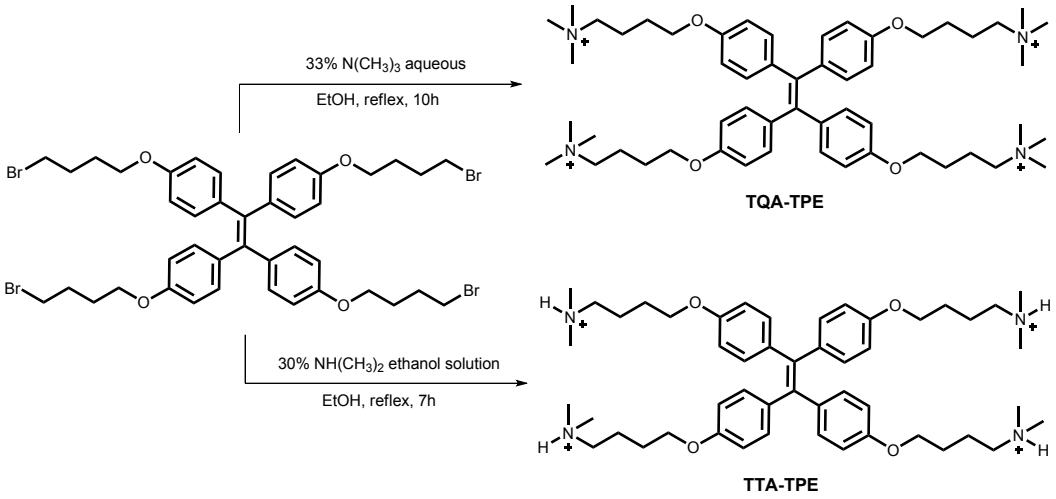


Figure S1. Synthetic routes of TQA-TPE and TTA-TPE.

2.2 ^{1}H NMR spectra of TQA-TPE and TTA-TPE.

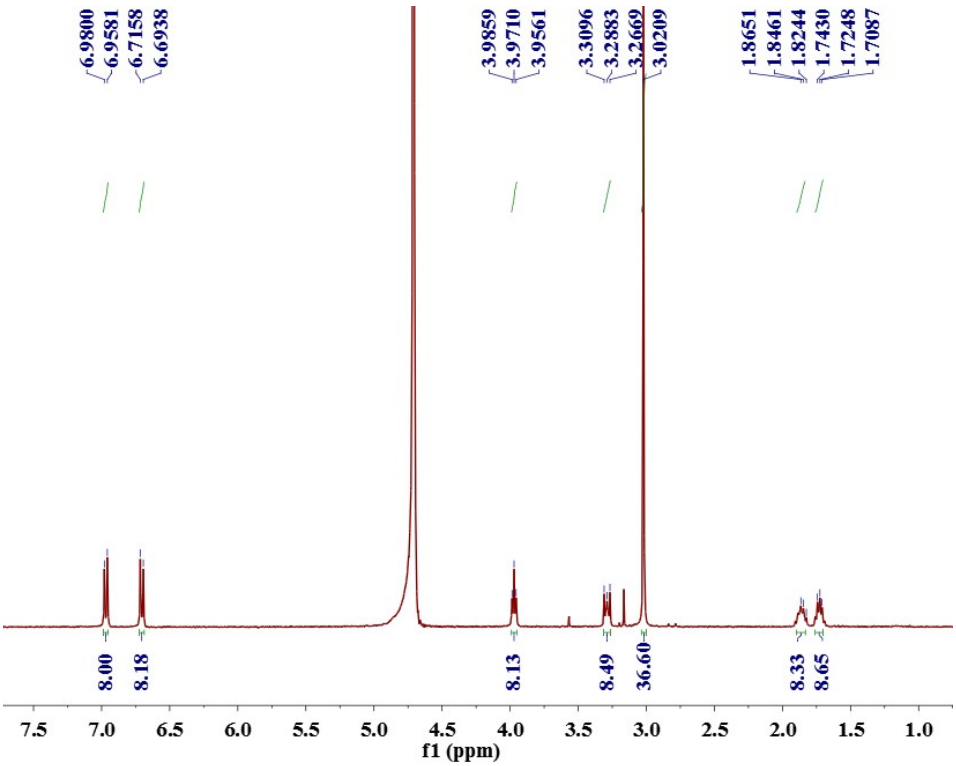


Figure S2. ^{1}H NMR spectrum of TQA-TPE in D_2O.

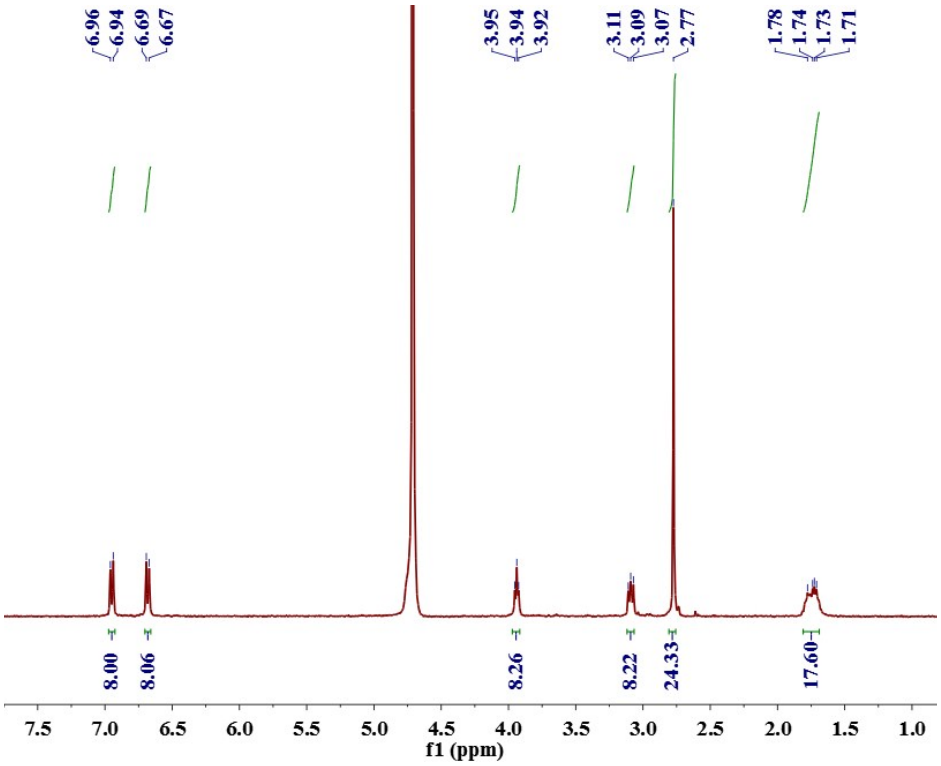


Figure S3. ^{1}H NMR spectrum of TTA-TPE in D_2O.

3. The self-assembly of free TQA-TPE

3.1 The critical aggregation concentration (CAC) of free TQA-TPE determined by DLS.

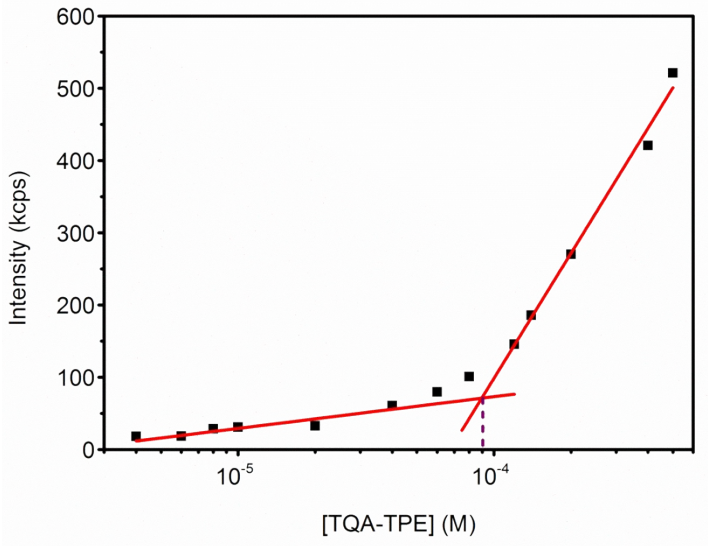


Figure S4. Dependence of light scattering intensity on the TQA-TPE concentration in water at 25°C.

3.2 DLS measurements of free TQA-TPE.

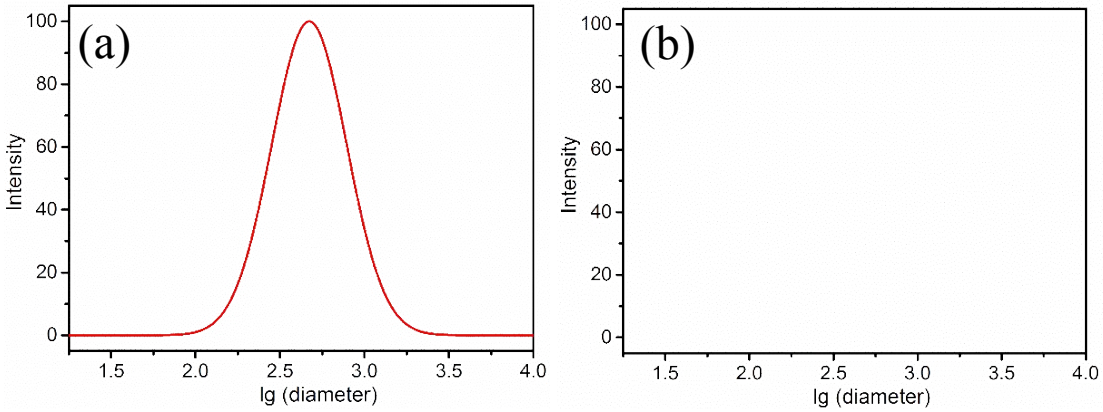


Figure S5. DLS measurements of free TQA-TPE at (a) 1.2×10^{-4} M and (b) 1.0×10^{-5} M.

4. The self-assembly of TQA-TPE in the presence of SC4A

4.1 The CAC of TQA-TPE in the presence of SC4A determined by DLS.

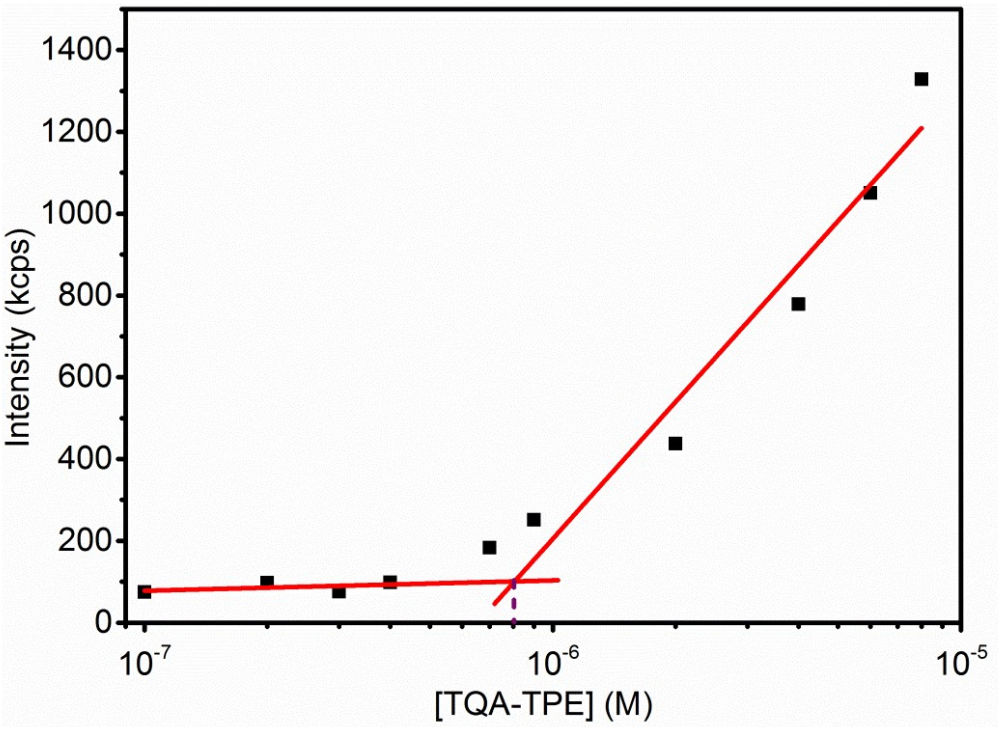
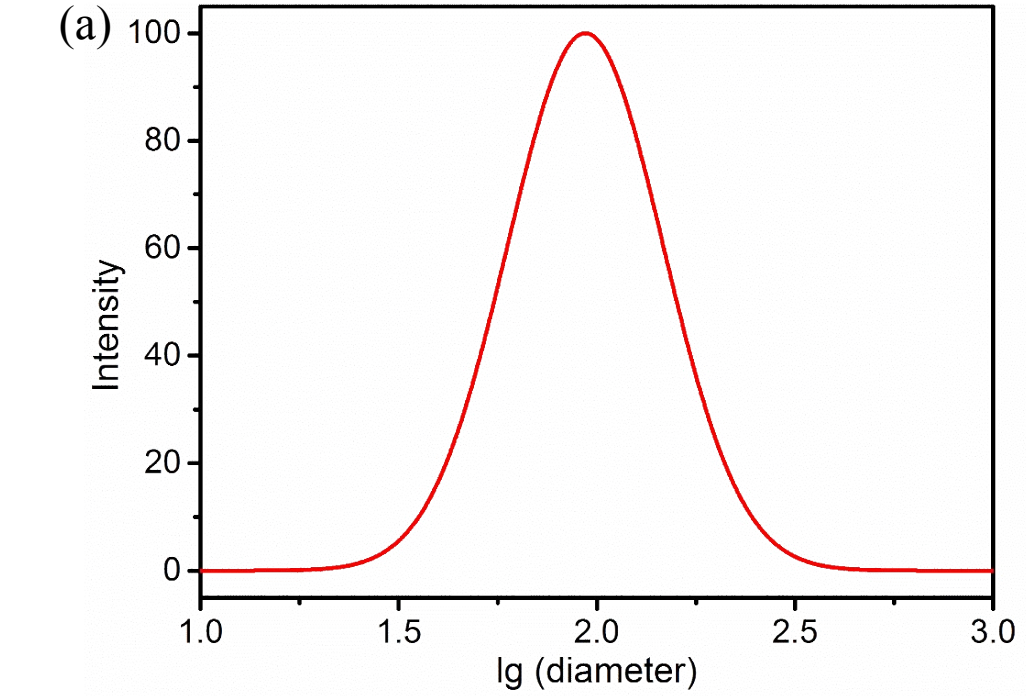


Figure S6. Dependence of light scattering intensity on the TQA-TPE concentration with SC4A at a 1:1 charge stoichiometry in water at 25 °C.

4.2 DLS measurements of TQA-TPE in the presence of SC4A.



(b)

Sample		Results	
Type:	DLS	Eff. Diam. (nm):	1,655.98
Sample ID:	1	Polydispersity:	0.368
Operator ID:	Unknown Operator		
SOP ID:	wyy		
Start Date/Time:	2015/5/25 16:13:16		
Notes:			

Correlation Function:

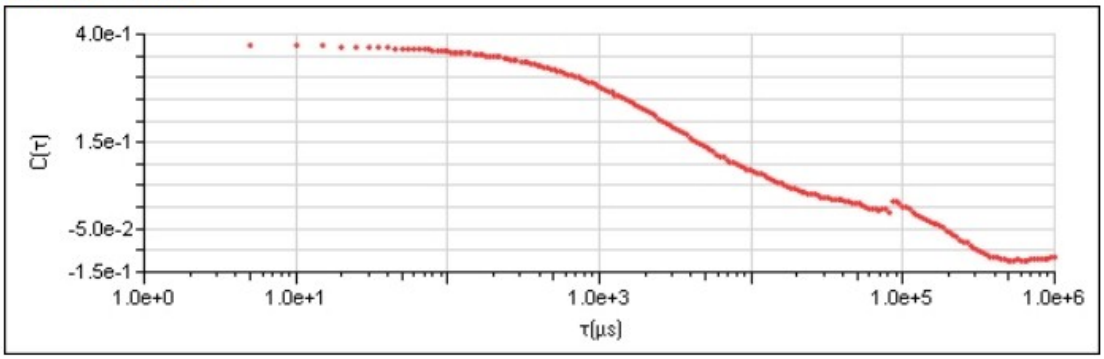


Figure S7. DLS measurements of TQA-TPE (1.0×10^{-5} M) with SC4A (a) at a 1:1 charge stoichiometry, (b) at a 1:9 charge stoichiometry, the disconnected correlation function indicates no credible signal appears.

5. The self-assembly of TQA-TPE in the presence of heparin

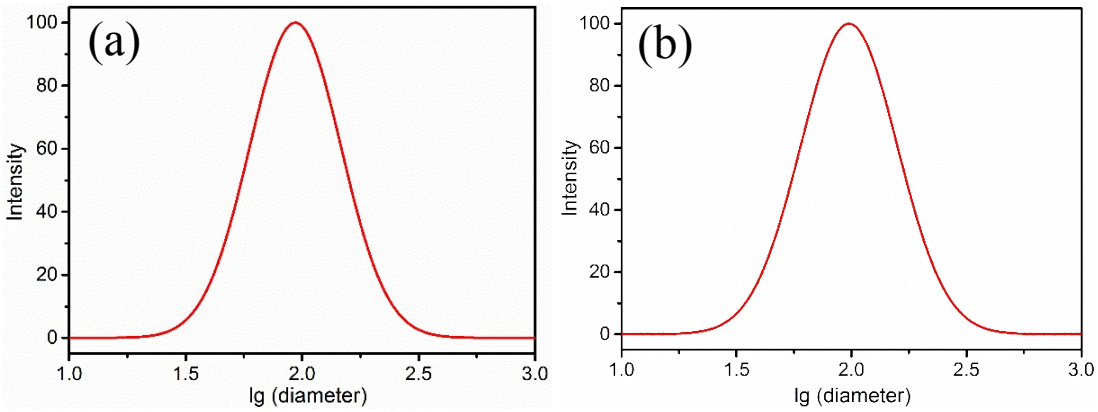


Figure S8. DLS measurements TQA-TPE (1.0×10^{-5} M) with heparin (a) at a 1:1 charge stoichiometry and (b) at a 1:9 charge stoichiometry.

6. Fluorescence spectra of TTA-TPE in the presence of different macrocycles

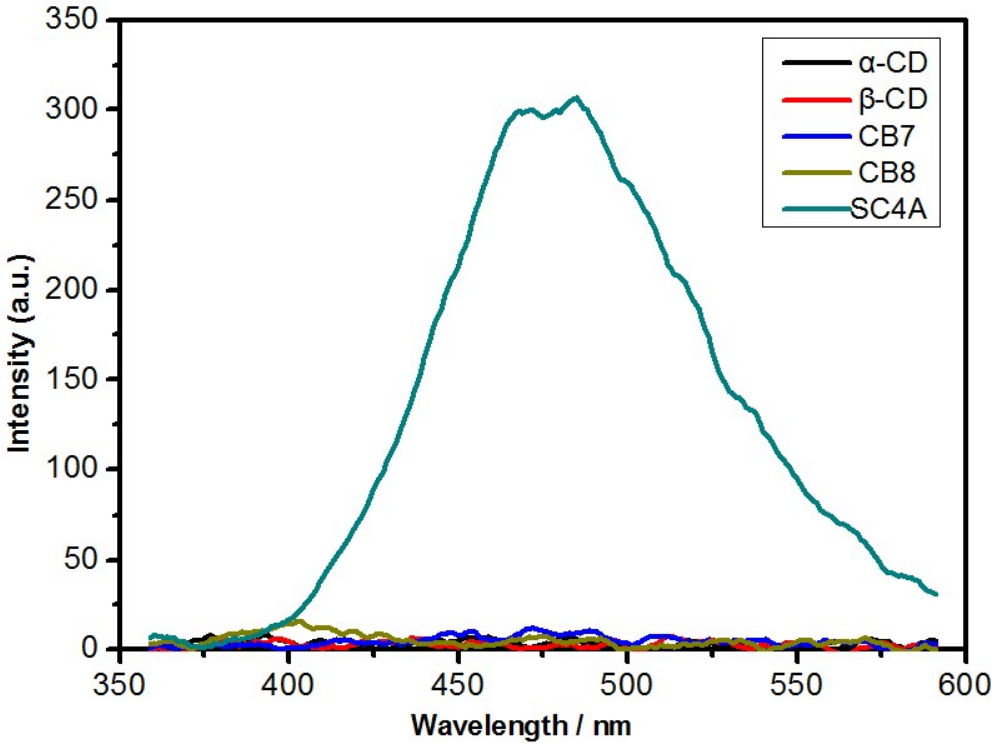


Figure S9. Fluorescence spectra of TTA-TPE (1.0×10^{-5} M) in the presence of α-CD (4.0×10^{-5} M), β-CD (4.0×10^{-5} M), CB7 (4.0×10^{-5} M), CB8 (4.0×10^{-5} M), SC4A (1.0×10^{-5} M) in water at 25 °C, λ_{ex} = 320 nm.

7. References

[1] S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki and O. Manabe, *J. Am. Chem. Soc.*, 1986, **108**, 2409.
[2] G. Arena, A. Contino, G. Lombardo and D. Sciotto, *Thermochim. Acta*, 1995, **264**, 1.
[3] B.-P. Jiang, D.-S. Guo, Y.-C. Liu, K.-P. Wang and Y. Liu, *ACS Nano*, 2014, **8**, 1609.