Electronic Supplementary Information

Multiple modulations for supramolecular hydrogels of Bola-form surfactants bearing rigid and flexible groups

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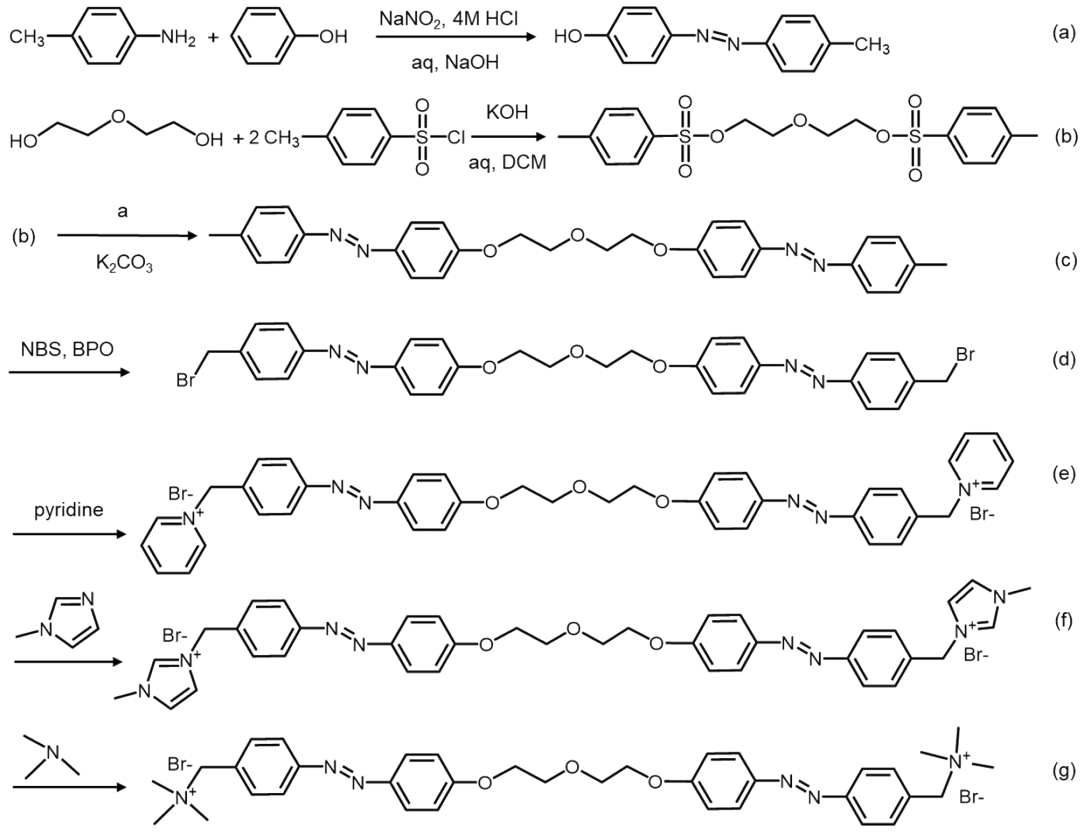
Content

Synthesis and procedures for intermediates of Bola-form surfactants.

The synthetic route for gelators used in the present study is summarized in Scheme S1 and detailed procedures of intermediate products are described in the following.



Scheme S1 Synthetic route for the Bola-form cationic surfactants.

Synthesis of 4-hydroxy-4'-methylazobenzene (a). A solution of p-toluidine (8.70 mg ,81.2 mmol) dissolved in deionized water (60 mL) with concentrated hydrochloric acid (18.4 mL) was cooled down to 0~5 ℃ and stirred for 20 min to make it dissolve completely. Then, sodium nitrite (6.20 g, 89.90 mmol) was dissolved in water (20 mL), and cooled down to 0~5℃ and stirred for 20 min. The sodium nitrite solution was added dropwise to the p-toluidine solution while keeping the temperature below 5℃. After additional stirring for 20 min, the yielded diazonium salt was filtered. Another solution of phenol (7.7 g, 81.80 mmol) and sodium hydroxide (3.20 g, 80 mmol) in water (50 mL) was cooled to 0~5℃ and added dropwise to the cold diazonium filtrate solution, yielding an orange precipitate. The mixture was stirred mechanically for another 2 h, acidized with diluted hydrochloric acid (1 M) to pH=3–5, and then filtered and rinsed with deionized water three times. The resultant crude product was recrystallized in H_2O/ethanol (4/1 in v/v) mixture solution, then dried in vacuum to give the pure product in orange solid (a) (yield 65%). ^{1}H NMR (500 MHz, DMSO-d_6, δ=ppm): 10.26 (s, 1H), 7.77 (d, J=10 Hz, 2H), 7.72 (d, J=10 Hz, 2H), 7.35 (d, J=10 Hz, 2H), 6.93 (d, J=10 Hz, 2H), 2.39 (s, 3H).

Synthesis of di-paratoluensulfonyl diethylene glycol diether (b). To the polyethylene glycol (30 mmol) dissolving in dichloromethane (30 mL) was added p-toluenesulfonyl chloride (60 mmol, 11.4 g). To the mixture that was cooled to 0 ^{o}C in an ice bath was added carefully powdered potassium hydroxide (240mmol, 45.6 g) in small portions, to make sure that the temperature maintained below 5 ^{o}C. After stirring for 3 h at the temperature, dichloromethane (30 mL) and ice-water (60 mL) were added. Organic layer was separated and the aqueous phase was extracted with dichloromethane in three portions (total 60 mL). The combined organic phase was washed with water (20 mL), dried over $MgSO_4$ and then evaporated to give the product (b) (yield 92%). ^{1}H NMR (500MHz, $CDCl_3$, δ=ppm): 7.79 (d, J=10Hz, 4H), 7.36 (d, J=10Hz, 4H), 4.09 (t, J=5 Hz, 4H), 3.60 (t, J=10 Hz, 4H), 2.45 (s, 6H).

Synthesis of di-(4'-methyl)phenylazophenoxyl diethylene glycol diether (c). To the acetonitrile (100 mL) solution with compound (a) (2.0 g, 9.42 mmol) and (b) (1.0 g, 4.28 mmol) was added K_2CO_3 (5.21 g, 37.69 mmol). The mixture was heated to reflux with stirring overnight under protection of nitrogen atmosphere. After cooling to room temperature, the formed precipitate was filtered off and rinsed with deionized water. The resultant crude product was purified by recrystallization in acetonitrile, and dried in vacuum to give an orange solid (c) (yield 83%). ^{1}H NMR (500 MHz, $CDCl_3$, δ=ppm):7.90 (d, J=10 Hz, 4H), 7.79 (d, J=10 Hz, 4H), 7.30 (d, J=10 Hz, 4H), 7.05 (d, J=10 Hz, 4H), 4.25 (d, J=10 Hz, 4H), 4.00 (d, J=10 Hz, 4H), 2.43 (s, 6H).

Synthesis of di-(4'-bromomethyl)phenylazophenoyl diethylene glycol diether (d). To a carbon tetrachloride (300 mL) that dissolved compound (c) (2 g, 4.04 mmol) and N-bromosuccinimide (NBS, 1.58 g, 8.88 mmol) was added benzoyl peroxide (BPO ,71.04 mg, 0.29 mmol) in order to start the reaction. The reaction was heated to reflux with stirring for 24 h. The resulting solid was filtered and washed with chloroform to give the product (d) (yield 88%). ^{1}H NMR (500MHz, $CDCl_3$, δ=ppm): 7.89 (d, J=10 Hz, 4H), 7.83 (d, J=10 Hz, 4H), 7.50 (d, J=10 Hz, 4H), 7.05 (d, J=10 Hz, 4H), 4.55 (s, 4H), 4.26 (t, J=5 Hz, 4H), 4.00 (t, J=10 Hz, 4H).

Structural characterizations of synthetic molecules.

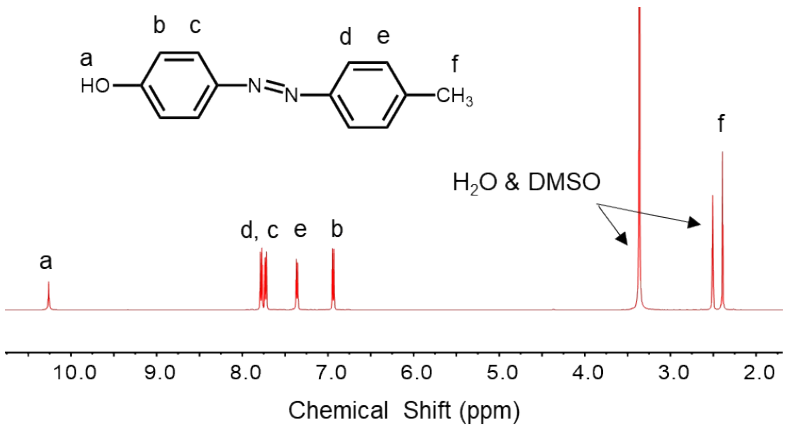


Fig. S1 ^{1}H NMR spectrum of 4-hydroxy-4'-methylazobenzene (a) in DMSO-d_6.

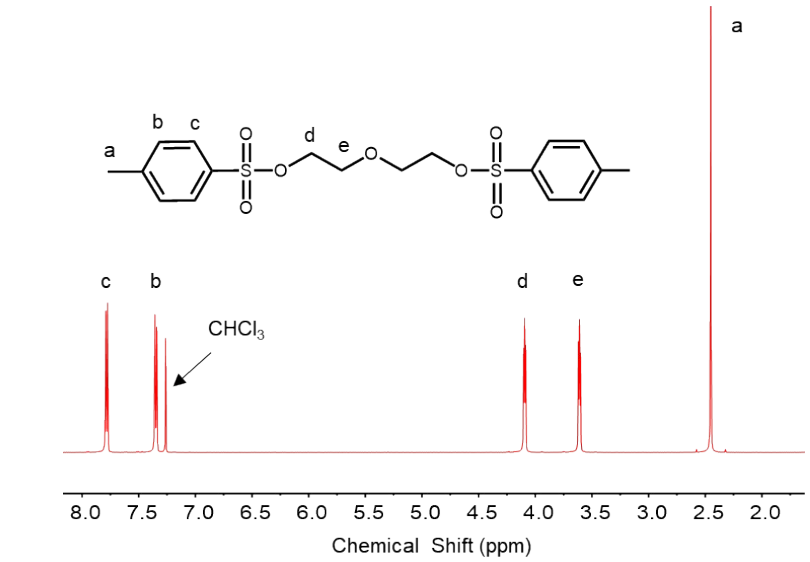


Fig. S2 ^{1}H NMR spectrum of di-paratoluensulfonyl diethylene glycol diether (b) in $CDCl_3$.

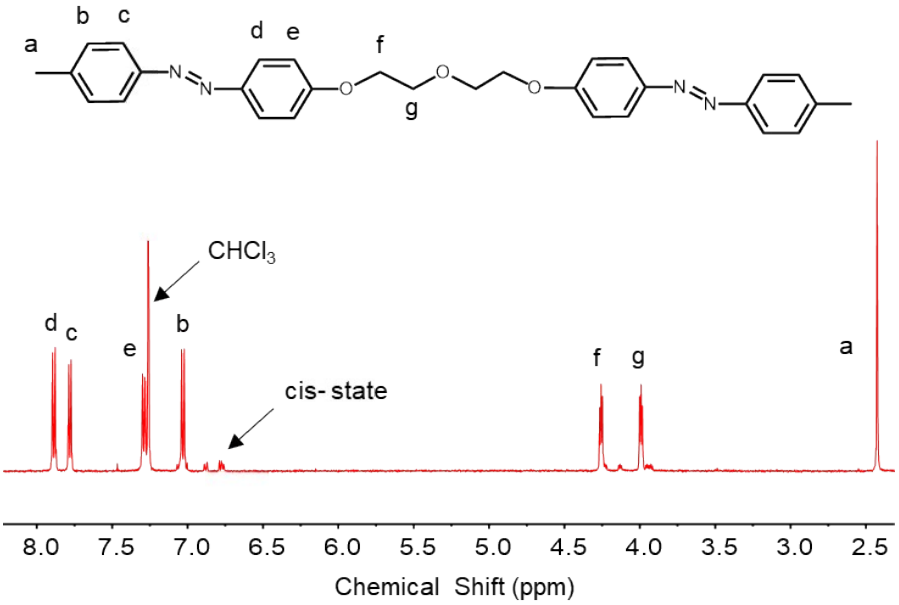


Fig. S3 ^{1}H NMR spectrum of di-(4'-methyl) phenylazophenoxyl diethylene glycol diether (c) in $CDCl_3$.

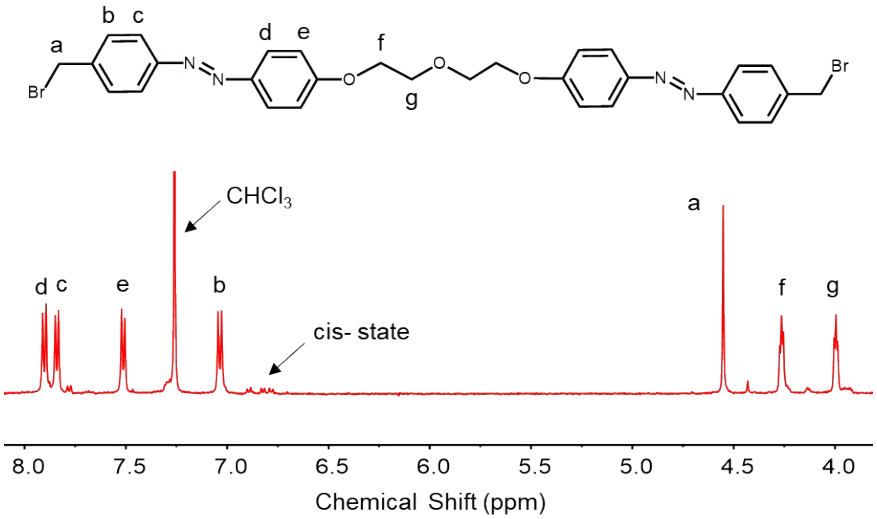


Fig. S4 ^{1}H NMR spectrum of di-(4'-bromomethyl) phenylazophenoyl diethylene glycol diether (d) in $CDCl_3$.

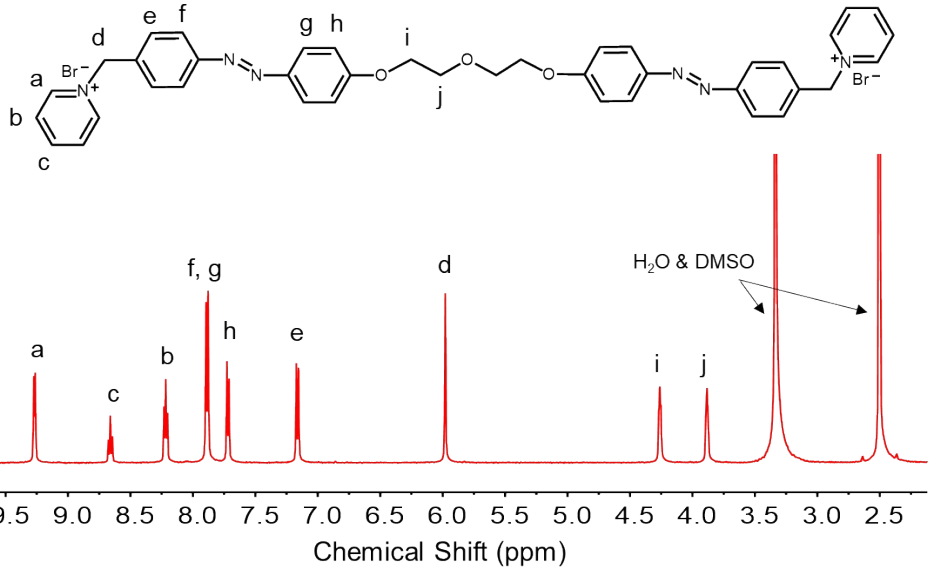


Fig. S5 ^{1}H NMR spectrum of Py-Azo (e) in DMSO-d_6.

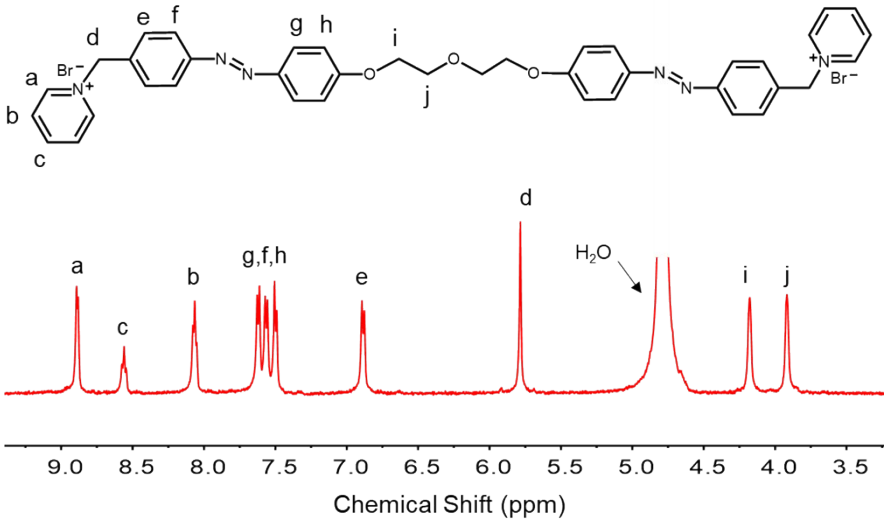


Fig. S6 ^{1}H NMR spectrum of Py-Azo (e) in D_2O.

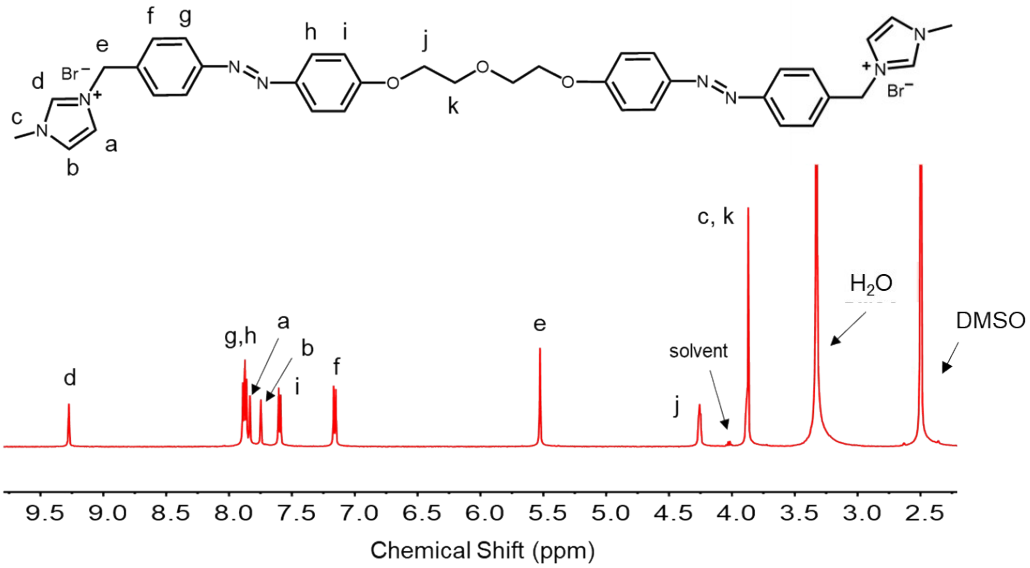


Fig. S7 ^{1}H NMR spectrum of MIM-Azo (f) in DMSO-d_6.

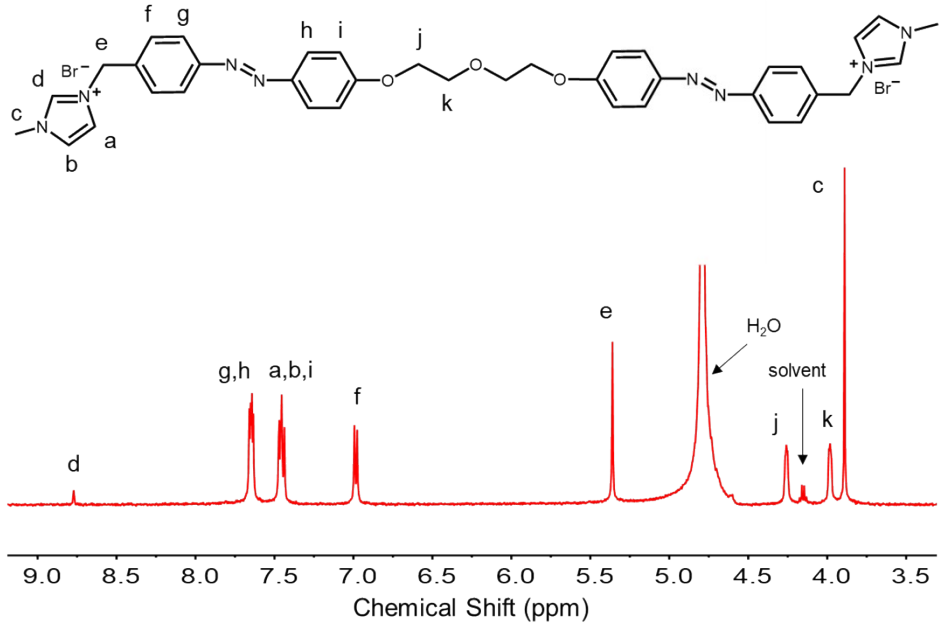


Fig. S8 ^{1}H NMR spectrum of MIM-Azo (f) in D_2O.

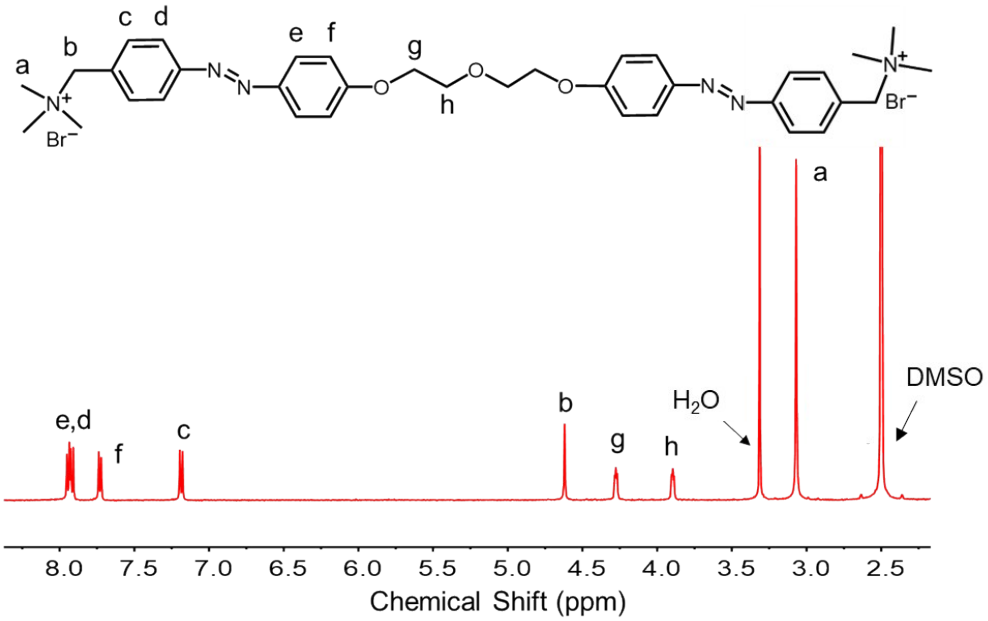


Fig. S9 ^{1}H NMR spectrum of TMA-Azo (g) in DMSO-d_6.

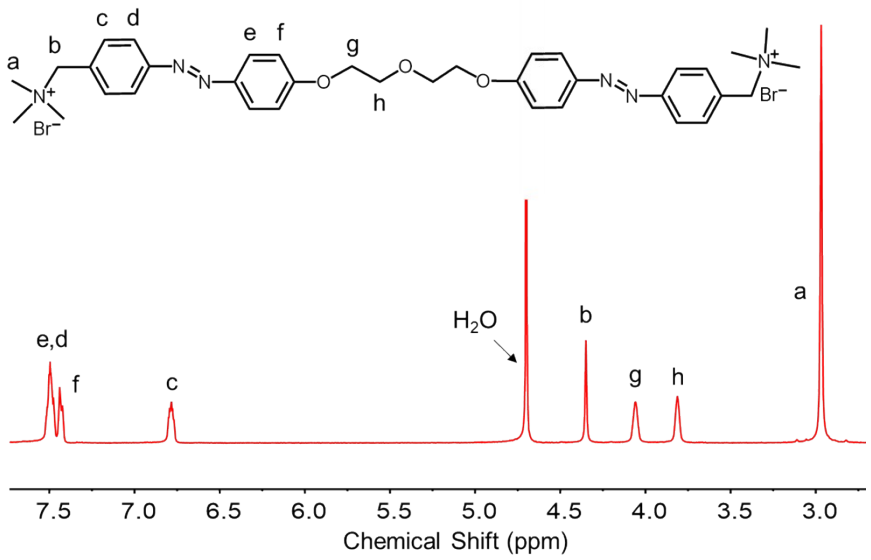


Fig. S10 ^{1}H NMR spectrum of TMA-Azo (g) in D_2O.

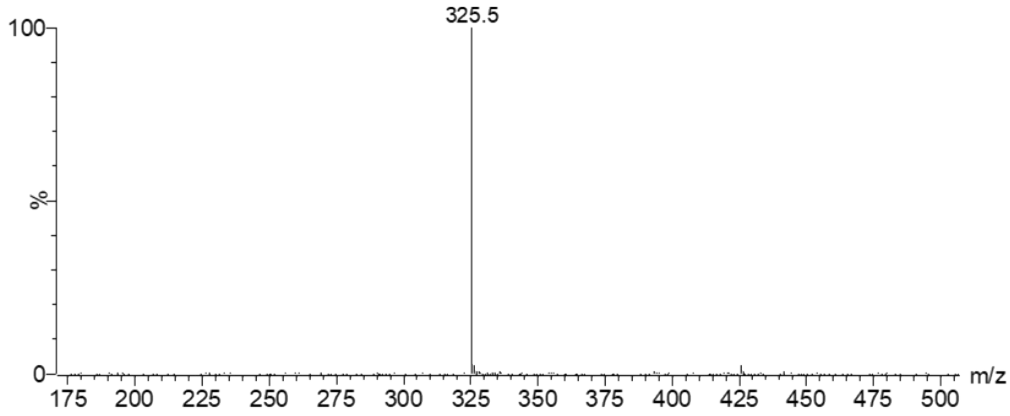


Fig. S11 ESI-MS spectrum of Py-Azo.

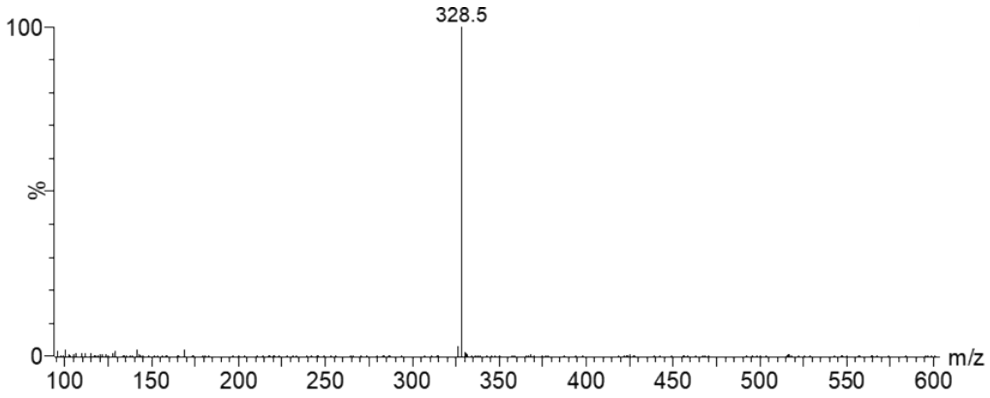


Fig. S12 ESI-MS spectrum of MIM-Azo.

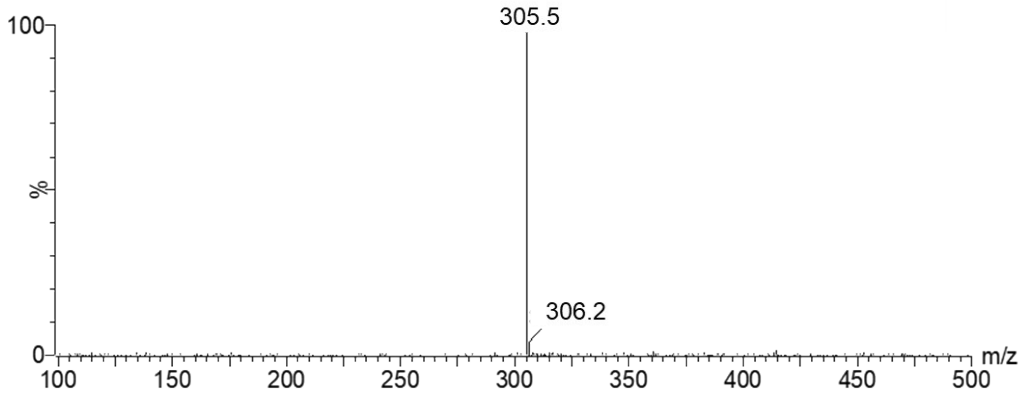


Fig. S13 ESI-MS spectrum of TMA-Azo.

Table S1 Summary of elemental analysis.

Molecule	Py-Azo ($C_{40}H_{38}Br_2N_6O_3$)			MIM-Azo ($C_{38}H_{40}Br_2N_8O_3$)			TMA-Azo ($C_{36}H_{46}Br_2N_6O_3$)		
Element	C (%)	H (%)	N (%)	C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
Found	58.95	5.18	10.22	56.35	5.38	13.89	56.45	6.50	11.12
Calculated	59.27	4.73	10.37	55.89	4.94	13.72	56.11	6.02	10.91

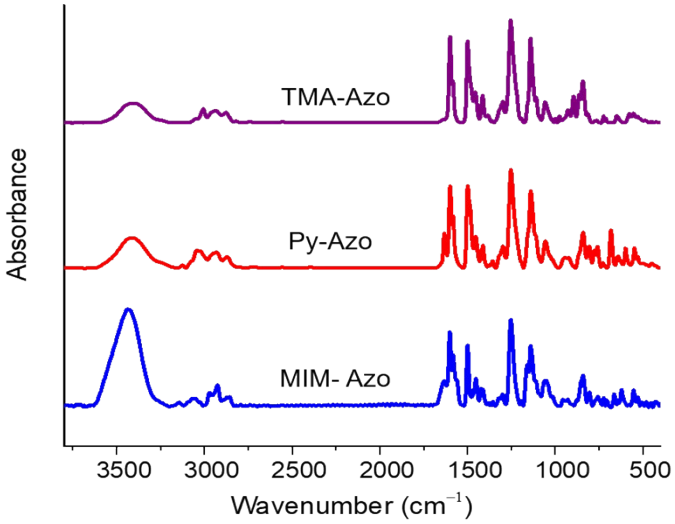


Fig. S14 IR spectra of synthetic surfactant molecules in KBr pellet.

Table S2. The assignments for main vibrations of synthetic surfactants in IR Spectra.[a]

TMA-Azo (cm^{-1})	Py-Azo (cm^{-1})	MIM-Azo (cm^{-1})	Assignment[1]
3012	3040	3057	Ar C−H str.
2931	2926	2928	CH_2 asym. str.
2881	2862	2860	CH_2 sym. str.
1600	1600	1595	C=C framework str.
1585	1580	1580	
1502	1491	1498	
1248	1246	1246	=C−O−C str.
1136	1132	1132	C−N str.
837	835	845	C−H str.

a: str.: stretching

Characterizations for gelation properties of synthetic molecules.

Table S3 Gelation ability of and CGC

Molecules	MIM-Azo	Py-Azo	TMA-Azo
Gelation	hydrogel	hydrogel	solution
CGC (wt%)	**0.74%**	**0.91%**	−

synthesized Bola-form surfactants at room temperature.

Table S4 Gelation property of Py-Azo and TMA-Azo mixtures at different weight ratios.[a,b]

Ratio C (wt%): Py-Azo: TMA-Azo	90:10	70:30	66:34	**65:35**	64:36	60:40
State	gel	gel	gel	**gel**	sol	sol
$C_{Py\text{-}Azo}$ (mg/mL) (wt%)	8.28 0.82	6.44 0.64	6.07 0.60	**5.98** **0.59**	5.89 0.58	5.52 0.54
$C_{TMA\text{-}Azo}$ (mg/mL) (wt%)	0.92 0.09	2.76 0.27	3.13 0.31	**3.22** **0.32**	3.31 0.33	3.68 0.37

a: The total concentration of Py-Azo and TMA-Azo is 9.2 mg/mL.

b: The measurement is performed at room temperature (22ºC).

Table S5 Gelation property of Py-Azo and TMA-Azo mixtures at different concentrations.[a,b]

C_{Total} (mg/mL)	9.20	9.00	8.50	**8.40**	8.30	8.00
State	gel	gel	gel	**gel**	sol	sol
$C_{Py\text{-}Azo}$ (mg/mL) (wt%)	6.44 0.64	6.30 0.63	5.95 0.59	**5.88** **0.58**	5.81 0.58	5.60 0.56
$C_{TMA\text{-}Azo}$ (mg/mL) (wt%)	2.76 0.27	2.70 0.26	2.55 0.25	**2.52** **0.24**	2.49 0.24	2.40 0.23

a: The weight ratio of Py-Azo:TMA-Azo is set at 7:3.

b: The measurement is performed at room temperature (22ºC).

Table S6 Gelation property of MIM-Azo and TMA-Azo mixtures at different weight ratios.[a,b]

Ratio C (wt%): MIM-Azo: TMA-Azo	90:10	70:30	60:40	**59:41**	58:42	55:45
State	gel	gel	gel	**gel**	sol	sol

$C_{MIM\text{-}Azo}$ (mg/mL) (wt%)	6.75 0.67	5.25 0.52	4.50 0.45	**4.43** **0.44**	4.35 0.43	4.13 0.41
$C_{TMA\text{-}Azo}$ (mg/mL) (wt%)	0.75 0.08	2.25 0.23	3.00 0.30	**3.08** **0.31**	3.15 0.32	3.38 0.34

a: The total concentration of MIM-Azo and TMA-Azo is 7.5mg/mL.

b: The measurement is performed at room temperature (22ºC).

Table S7 Gelation property of MIM-Azo and TMA-Azo mixtures at different concentrations.[a,b]

C_{Total} (mg/mL)	7.50	6.50	6.00	**5.90**	5.80	5.50
State	gel	gel	gel	**gel**	sol	sol
$C_{MIM\text{-}Azo}$:(mg/mL) (wt%)	5.25 0.52	4.55 0.45	4.20 0.42	**4.13** **0.41**	4.06 0.40	3.85 0.38
$C_{TMA\text{-}Azo}$:(mg/mL) (wt%)	2.25 0.23	1.95 0.20	1.80 0.18	**1.77** **0.18**	1.74 0.18	1.65 0.17

a: The weight ratio of MIM-Azo:TMA-Azo is set at 7:3.

b: The measurement is performed at room temperature (22ºC).

Table S8 Gelation property of Py-Azo and MIM-Azo mixtures versus total concentration.[a,b]

Total C (mg/mL)	9.20	8.00	7.50	**7.20**	7.10	7.00
State	gel	gel	gel	**gel**	sol	sol
$C_{Py\text{-}Azo}$ (mg/mL) (wt%)	4.60 0.46	4.00 0.40	3.75 0.38	**3.60** **0.36**	3.55 0.36	3.50 0.35
$C_{MIM\text{-}Azo}$ (mg/mL) (wt%)	4.60 0.46	4.00 0.40	3.75 0.38	**3.60** **0.36**	3.55 0.36	3.50 0.35

a: The weight ratio of Py-Azo and MIM-Azo is set at 1:1.

b: The measurement is performed at room temperature (22ºC).

Table S9 Gel stability of Py-Azo and MIM-Azo against pH.[a,b]

	Initial pH	V (diluted HCL)	Final pH	Status
Py-Azo	7	**5 µL**	**5**	**gel**
		7 µL	4	sol

		10 μL	3	sol
		13 μL	2	sol
MIM-Azo	7	5 μL	5	gel
		7 μL	**4**	**gel**
		10 μL	3	sol
		13 μL	2	sol

a: The concentration of Py-Azo is 9.2 mg/mL and the concentration of MIM-Azo is 7.5 mg/mL.

b: The measurement is performed at room temperature (22ºC).

Table S10 Gel stability of Py-Azo and MIM-Azo against additives.[a,b,c]

	NaCl	Ada-N	Ada-C	Ben-C	$CoMo_6$	$NiMo_6$	p-Ben	d-Oxa
Py-Azo (gel)	**sol**	**sol**	**sol**	**sol**	P	P	P	P
MIM-Azo (gel)	**sol**	**sol**	**sol**	**sol**	P	P	P	P
TMA-Azo (solution)	-	-	-	-	-	T	-	-

a: The concentrations of Py-Azo, MIM-Azo, and TMA-Azo are set 9.2, 7.5, and 9.2 mg/mL, respectively, while the concentrations of additives are in molar ratio of 1:2.2.

b: Ada-N: 1-adamantane amine hydrochloric acid;

Ada-C: sodium 1-adamantante carboxylate;

Ben-C: sodium benzoate;

$CoMo_6$: $(NH_4)_2\{CoMo_6O_{16}(OH)_2[CH_3C(CH_2O)_3]_2\}\cdot 2H_2O$

$NiMo_6$: $(NH_4)_2\{NiMo_6O_{16}(OH)_2[CH_3C(CH_2O)_3]_2\}\cdot 2H_2O$;

p-Ben: disodium p-phthalate;

d-Oxa: disodium oxalate.

P: precipitate; T: turbid; -: no obvious change.

c: The measurement is performed at room temperature (22ºC).

Characterizations for assembled morphology and structure of synthetic molecules in solution.

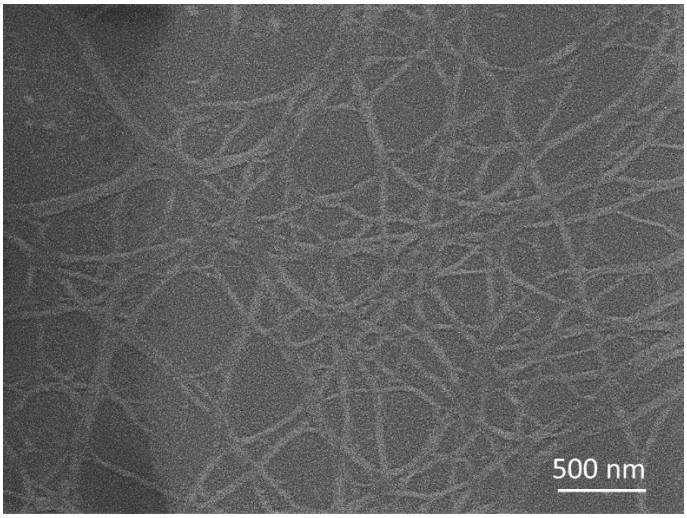


Fig. S15 SEM image of Py-Azo self-assembly in aqueous solution under the concentration of 0.40 mg/mL (5×10^{-4} mol/L).

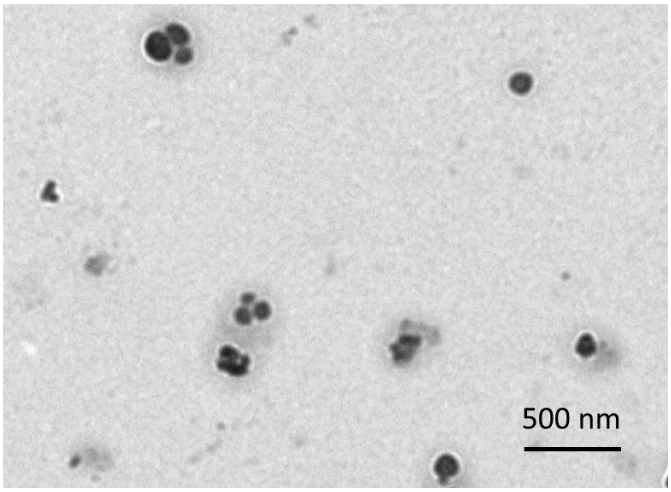


Fig. S16 TEM image of TMA-Azo self-assembly in aqueous solution under the concentration of 20.0 mg/mL (2.0 wt%).

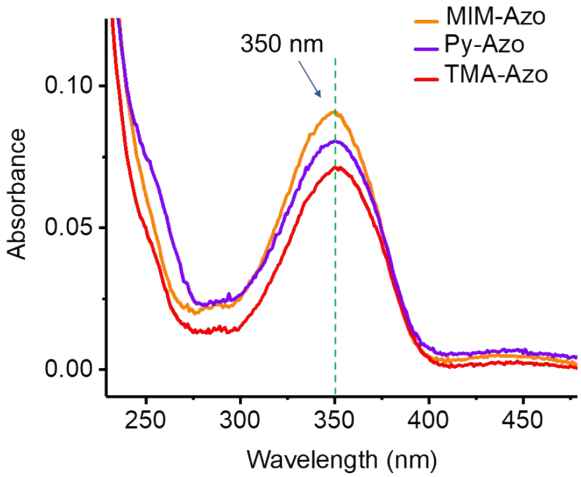


Fig. S17 UV-Vis spectra of prepared Bola-form surfactants in MeOH at the concentration of 2.24 $\times 10^{-6}$ mol L^{-1}.

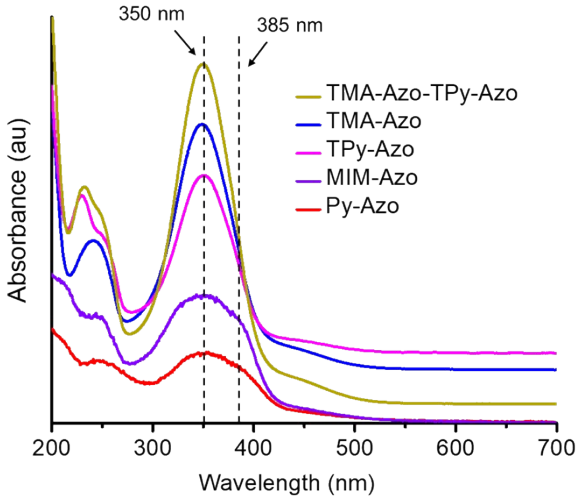


Fig. S18 UV-Vis spectra of Py-Azo (0.91wt%) and MIM-Azo (0.74 wt %) at hydrogel state, and TMA-Azo (2.00 wt%), TPy-Azo (2.00 wt%) and TMA-Azo and TPy-Azo mixture (2.00 wt%) at solution state, where TPy-Azo represents the abbreviation of surfactant shown in Fig. S21.

Characterizations for photo-modulation of gels' stimulus-response.

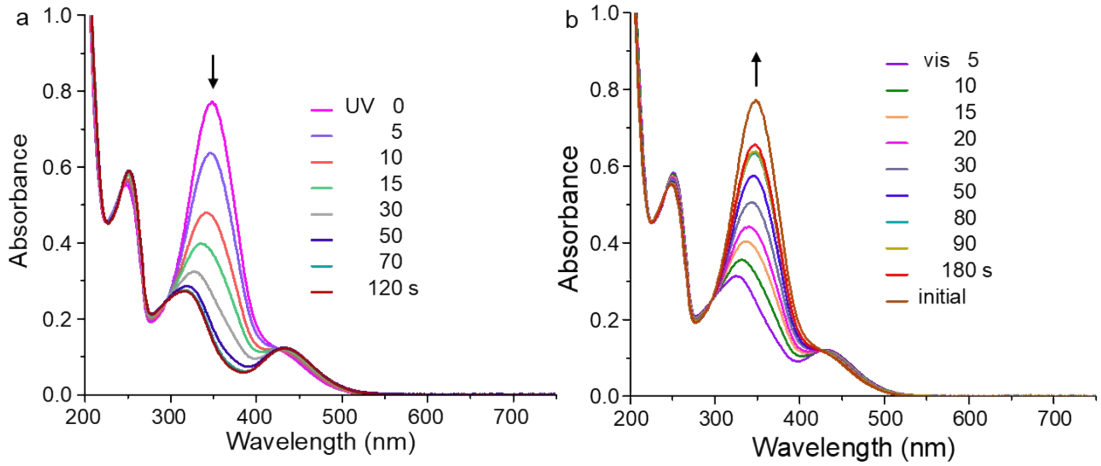


Fig. S19 UV-Vis spectra of Py-Azo in aqueous solution (5×10^{-5} mol L^{-1}) under different irradiation time upon (a) UV light (365 nm) irradiation and (b) visible light (450 nm) irradiation at room temperature (25ºC).

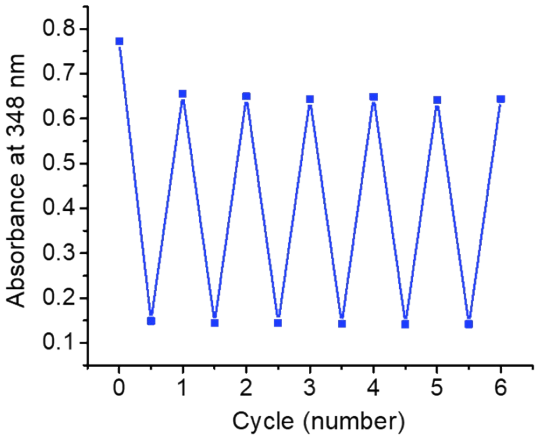


Fig. S20 Absorbance change of Py-Azo at λ_{max} = 348 nm in aqueous solution upon cycles of alternate irradiations with UV (365 nm) and visible (450 nm) light.

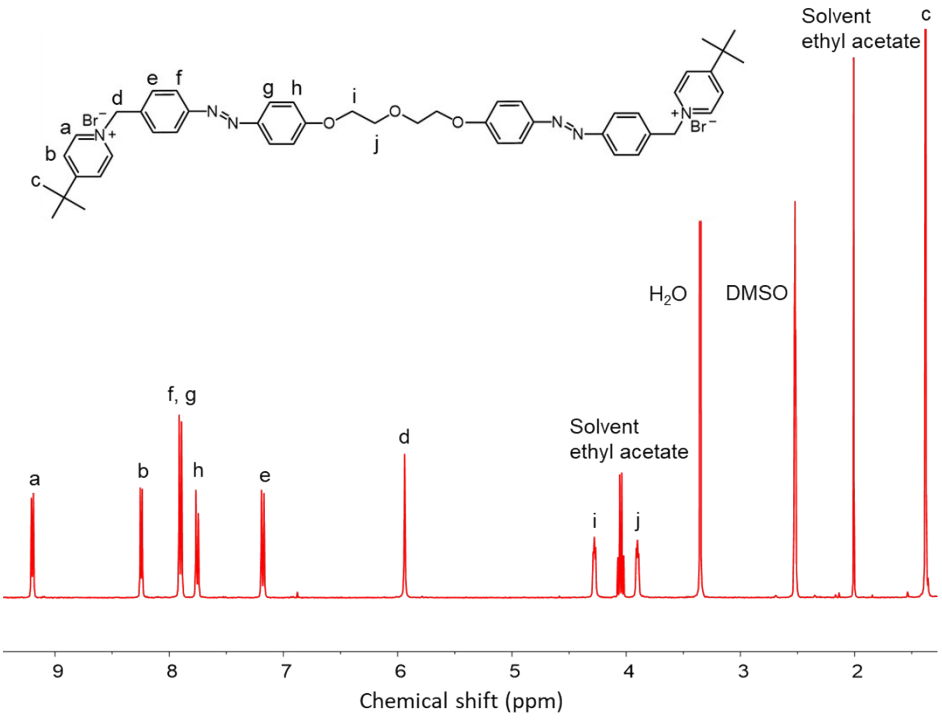


Fig. S21 ^{1}H NMR spectrum of TPy-Azo in DMSO-d6.

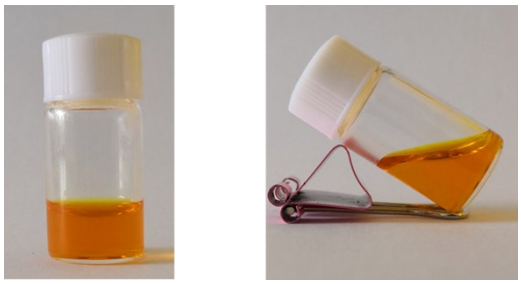


Fig. S22 Photographs of TPy-Azo (4.3%) in aqueous solution.

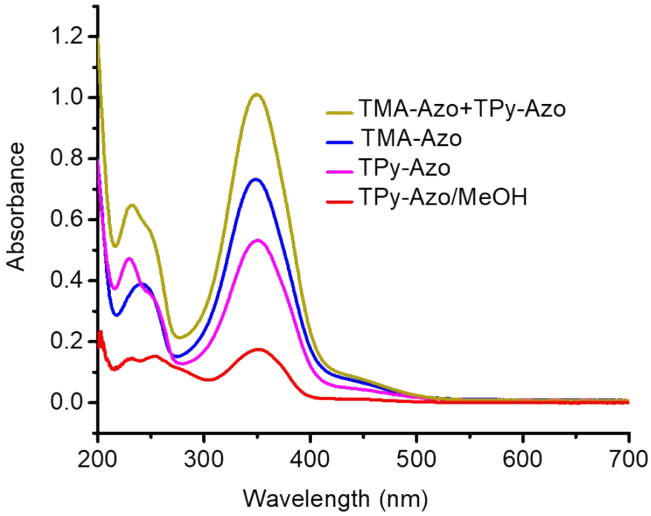


Fig. S23 UV-Vis spectra of TPy-Azo (2.24×10^{-6} M) in MeOH, Tpy-Azo (2.0 wt%), TMA-Azo (2.0 wt%), and TMA-Azo/Tpy-Azo mixture (2.0 wt%) in aqueous solution.

Reference:

1. Y. Yang, B. Zhang, Y. Z. Wang, L. Yue, W. Li and L. X. Wu, *J. Am. Chem. Soc.*, 2013, **135**, 14500─14503.