Supplementary Information (SI) for Nanoscale.
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Supporting Information

Chiral co-assembly of a polyoxometalate complex with an achiral pyrene derivative enables redox-modulated circularly polarized luminescence

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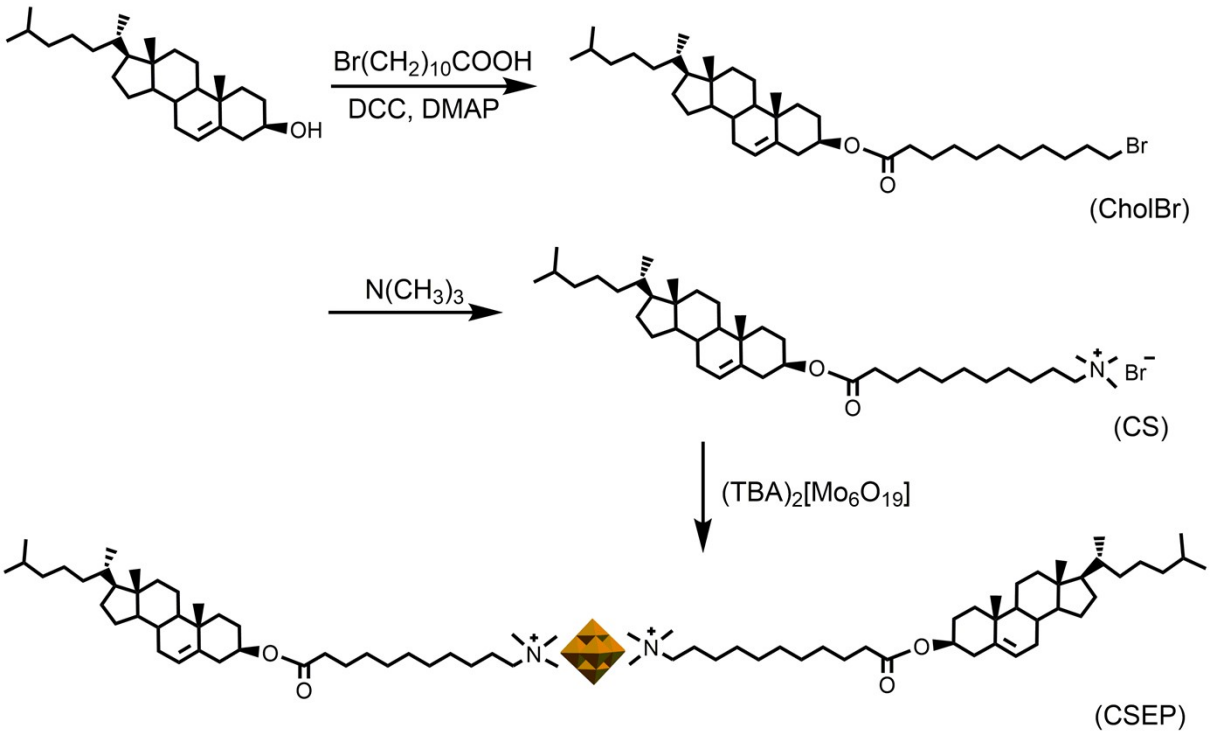

Figure S1. Synthetic route for chiral surfactant encapsulated polyoxometalate (CSEP) complex by ion-exchange encapsulation of polyoxometalate with cholesterol-containing chiral surfactants.

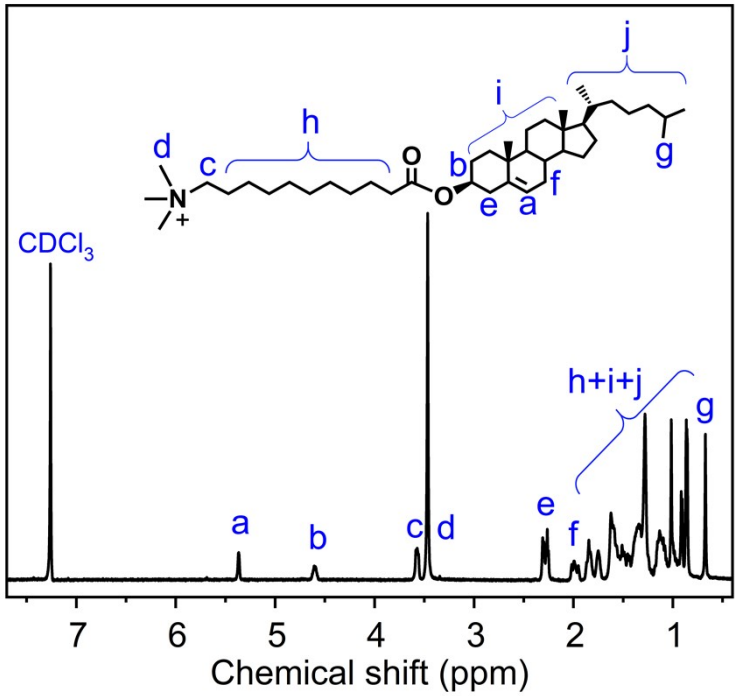

Figure S2. ^{1}H NMR spectrum of CS in $CDCl_3$.

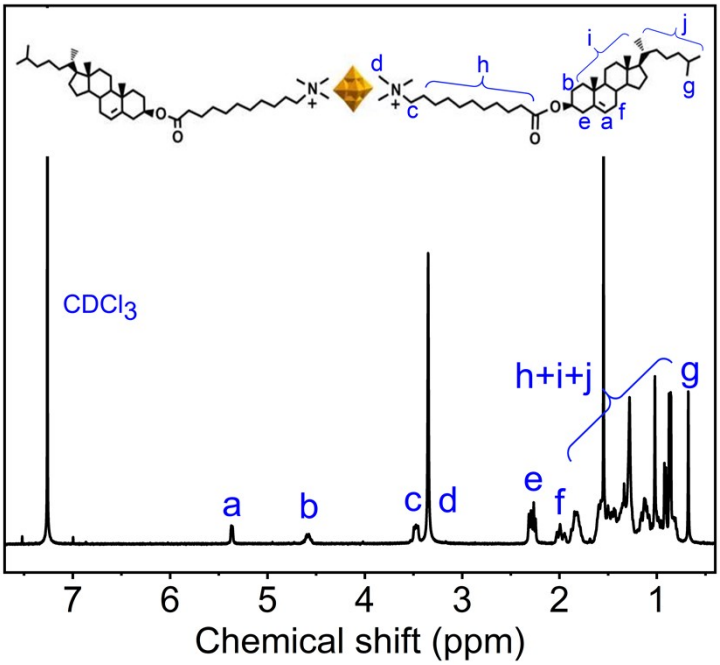

Figure S3. ^{1}H NMR spectrum of CSEP in $CDCl_3$.

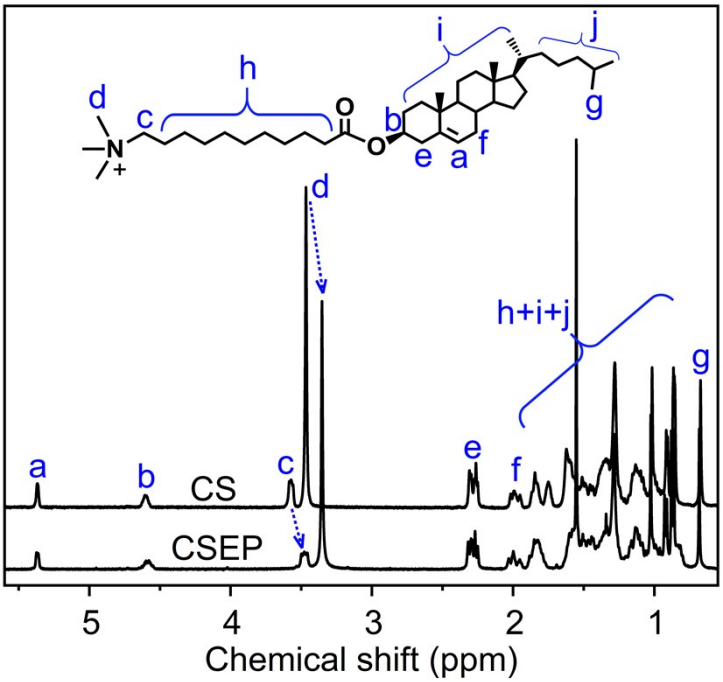

Figure S4. ^{1}H NMR spectra of CS and CSEP in $CDCl_3$.

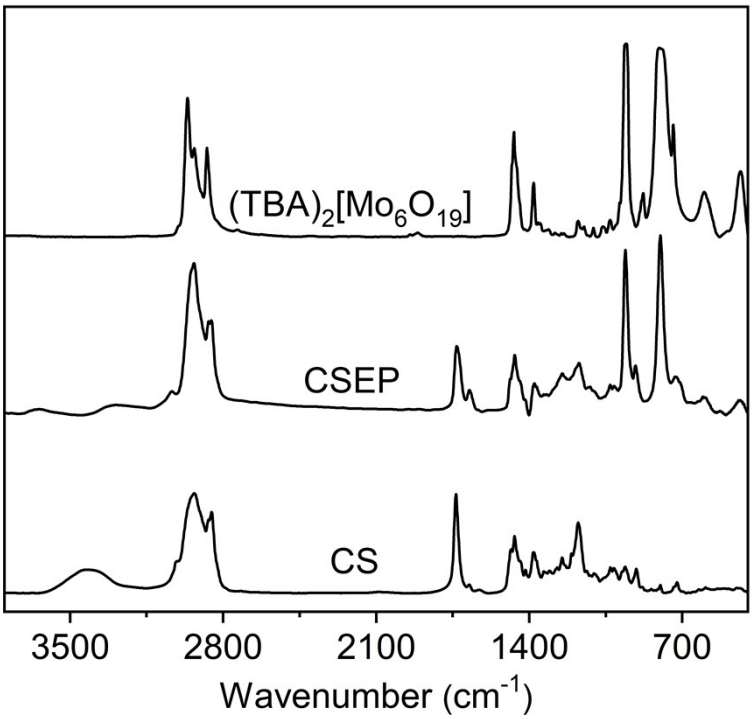

Figure S5. IR spectra of $(TBA)_2[Mo_6O_{19}]$, CSEP, and CS.

Table S1. Characteristic IR vibration assignments of $(TBA)_2[Mo_6O_{19}]$, CSEP, and CS.

$(TBA)_2[Mo_6O_{19}]$ (cm^{-1})	CSEP (cm^{-1})	CS (cm^{-1})	Assignments
	3034	3420	O–H asymmetric stretching
2962	2964	2967	CH_3 asymmetric stretching
2932	2934	2932	CH_2 asymmetric stretching
2874	2854	2853	CH_2 symmetric stretching
	1732	1736	–C=O stretching
	1487		CH_2–N^+ scissoring
1469	1466	1468	CH_2 scissoring
1381	1377	1381	CH_3 scissoring
	1250	1250	C–O–C asymmetrical stretching
	1173	1177	C–N stretching
	1030	1030	=C–O–C asymmetrical stretching
957	957		$\nu_{as}(Mo–O_t)$
806	798		$\nu_{as}(Mo–O_b)$
600	598		$\delta(O_b–Mo–O_t)$
434	434		$\delta(O_b–Mo–O_t)$

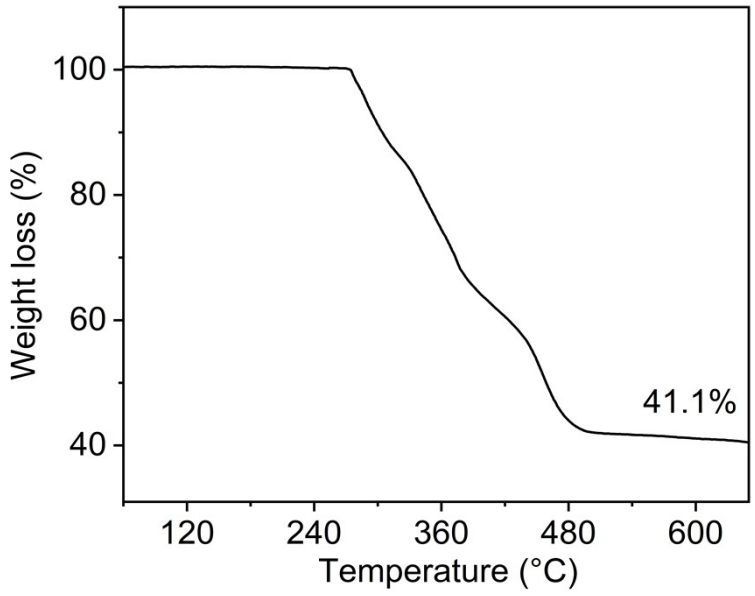

Figure S6. TGA curve of CSEP in air, the residual mass was 41.1% at 600℃, which was consistent with the calculated residual mass of $C_{82}H_{148}N_2Mo_6O_{23}$ (41.0%).

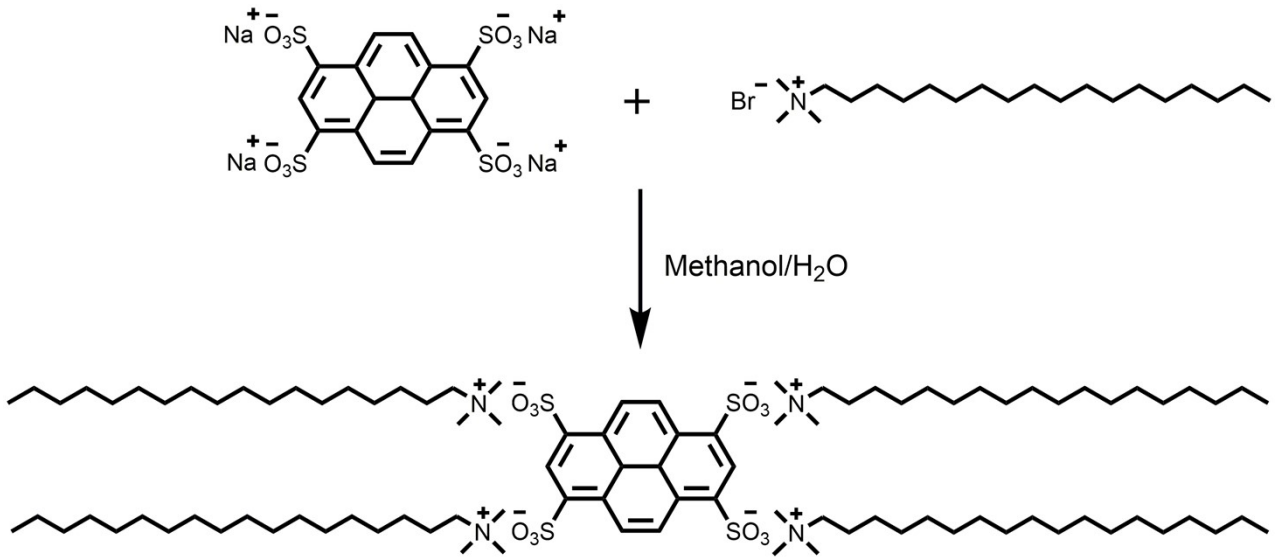

Figure S7. Synthetic route for the achiral pyrenyl fluorophore (Py) through ionic self-assembly of 1,3,6,8-pyrene tetrasulfonic acid tetrosodium salt with oppositely charged surfactant.

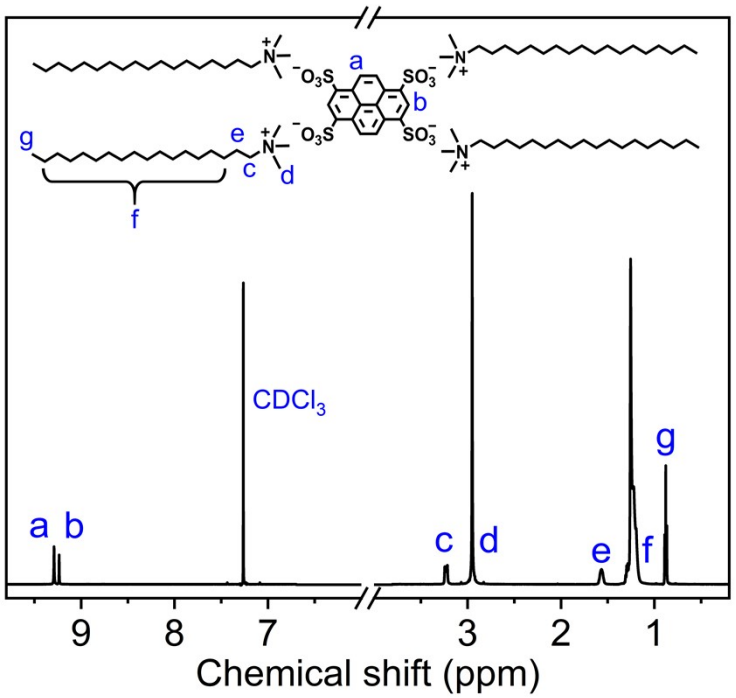

Figure S8. ^{1}H NMR spectrum of Py in $CDCl_3$.

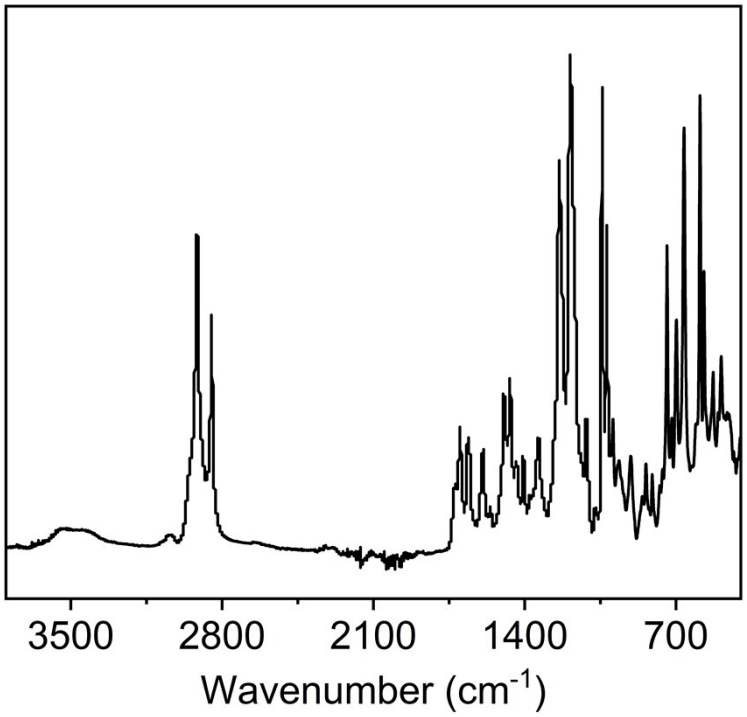

Figure S9. IR spectrum of Py in KBr pellet.

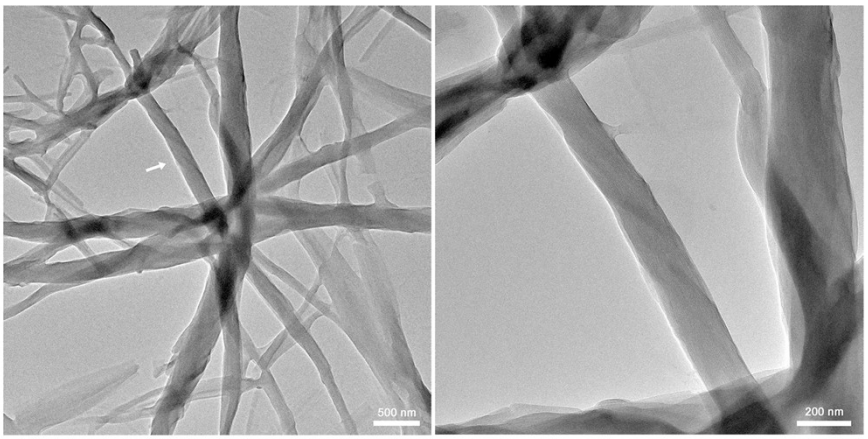

Figure S10. TEM images of CSEP (1 mg·mL^{-1}) in the mixed solvents of dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v).

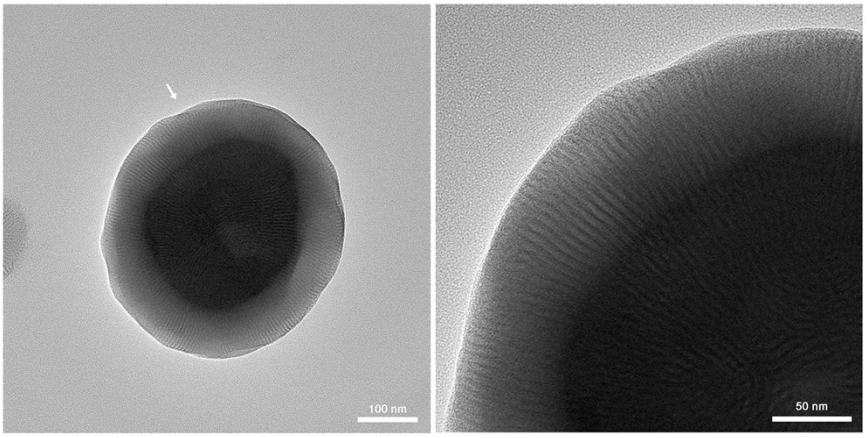

Figure S11. TEM images of CSEP (1 mg·mL^{-1}) in the mixed solvents of dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) after UV irradiation for 10 min.

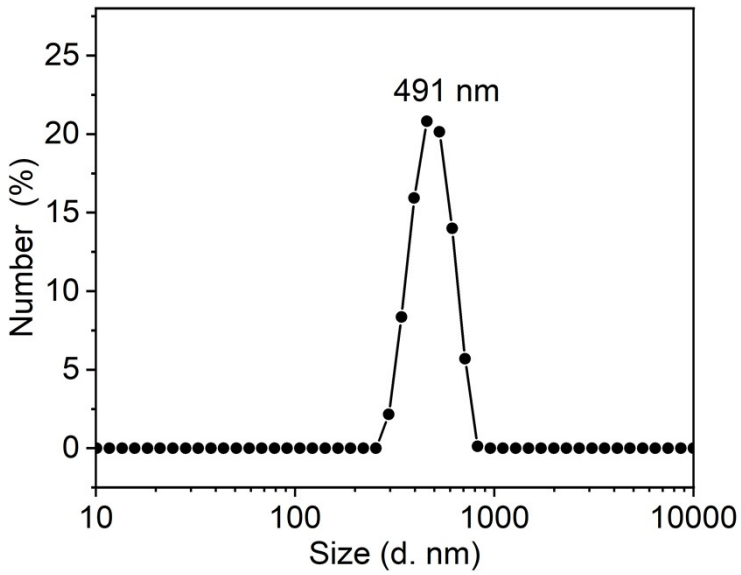

Figure S12. DLS result of CSEP in dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) solution after UV irradiation for 10 min.

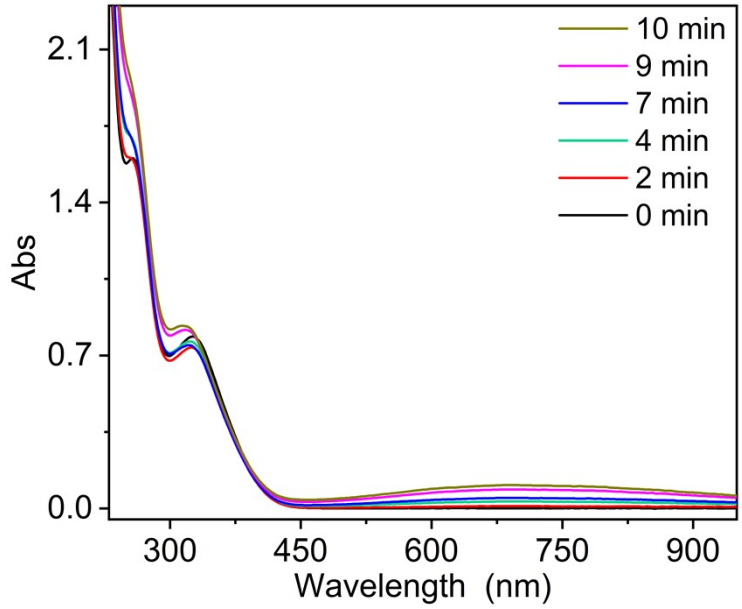

Figure S13. UV-vis spectra of CSEP in dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) under different UV irradiation times.

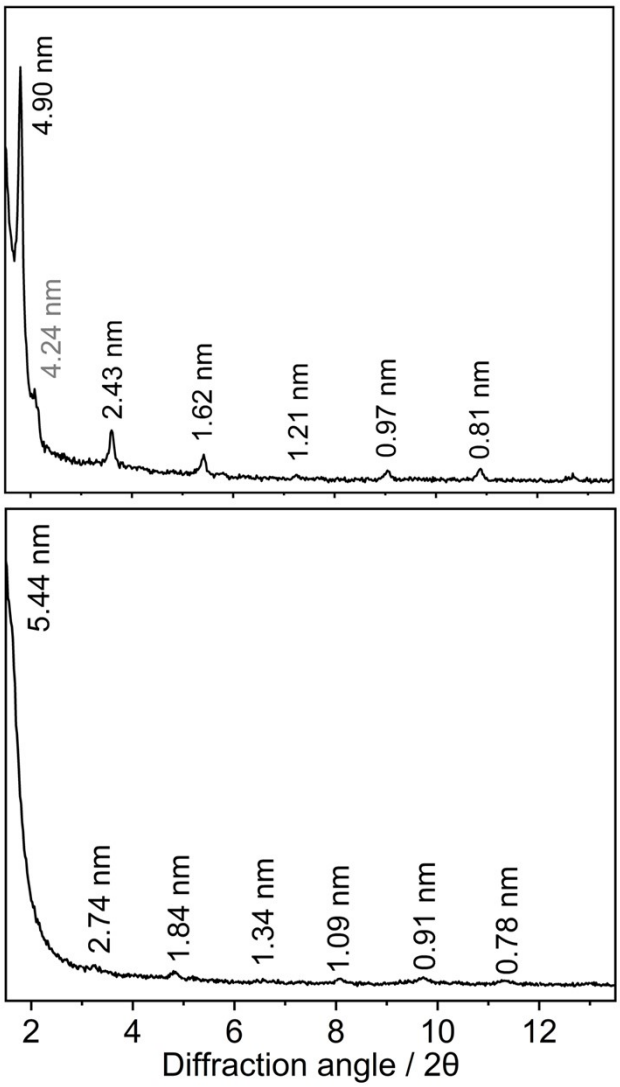

Figure S14. XRD patterns of the helical assemblies of CSEP at the initial state (top) and the spherical aggregates of CSEP after UV irradiation (bottom).

Table S2. X-ray data of helical assemblies of CSEP at the initial state.

2θ/°	1.80	3.62	5.43	7.24	9.04	10.88
d/nm	4.90	2.43	1.62	1.21	0.97	0.81
hkl	001	002	003	004	005	006

The weak peak at 2.08 corresponds to the in-plane structure with low ordering.

Table S3. X-ray data of the spherical aggregates of CSEP after UV irradiation.

2θ/°	1.62	3.22	4.8	6.56	8.08	9.70	11.3
d/nm	5.45	2.74	1.84	1.34	1.09	0.91	0.78
hkl	001	002	003	004	005	006	007

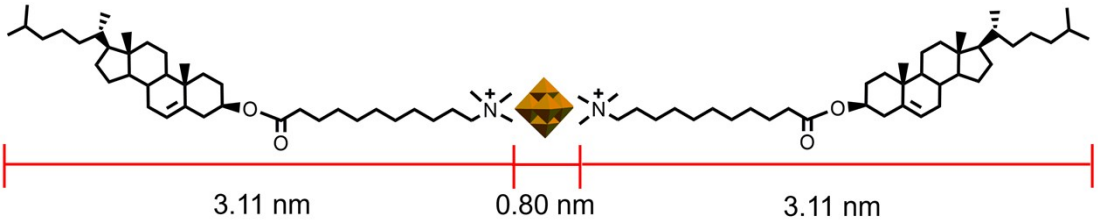

Figure S15. The estimated length of CSEP with sandwich structure.

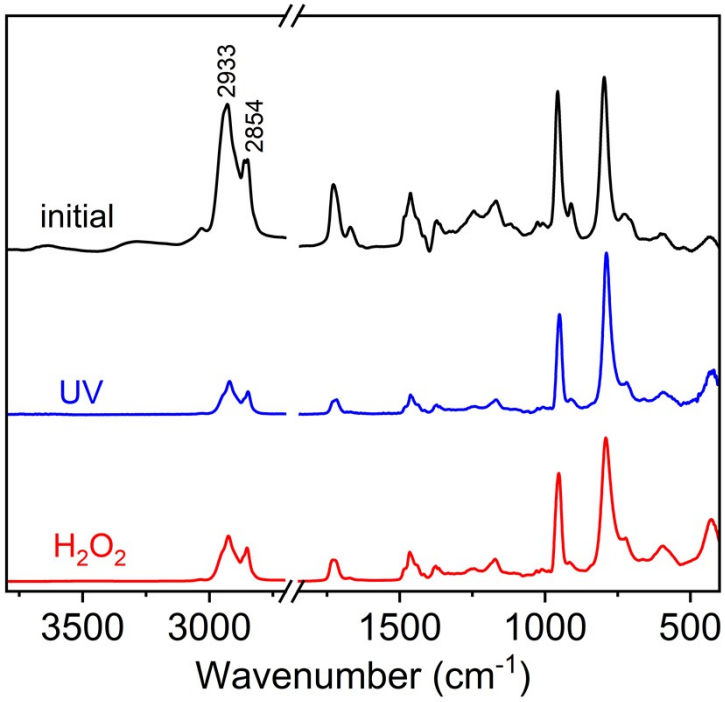

Figure S16. FT-IR spectra of CSEP at the initial state (black), after UV irradiation (blue), and following H_2O_2 oxidation (red) in KBr pellet.

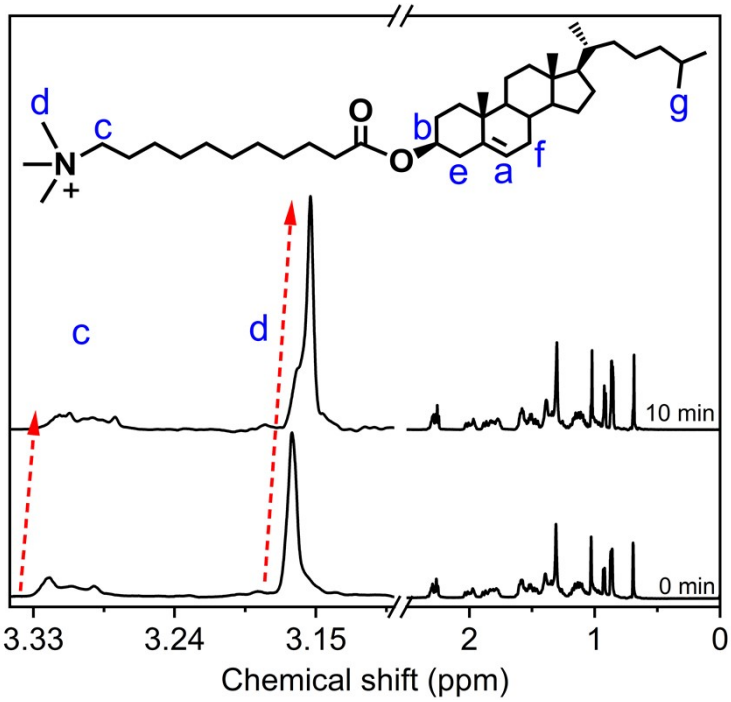

Figure S17. ^{1}H NMR spectra of CSEP in its initial state and under UV irradiation for 10 minutes in $CD_2Cl_2/CD_3OD/CD_3CN$ (10/1/1 v/v/v).

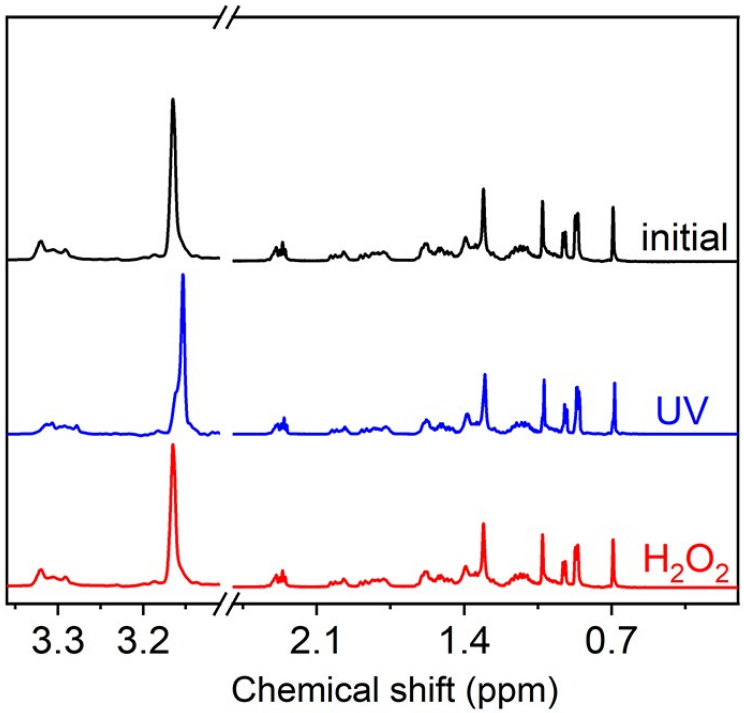

Figure S18. ^{1}H NMR spectra of CSEP initial (black), after UV irradiation (blue), and after H_2O_2 oxidation (red) in $CD_2Cl_2/CD_3OD/CD_3CN$ (10/1/1 v/v/v).

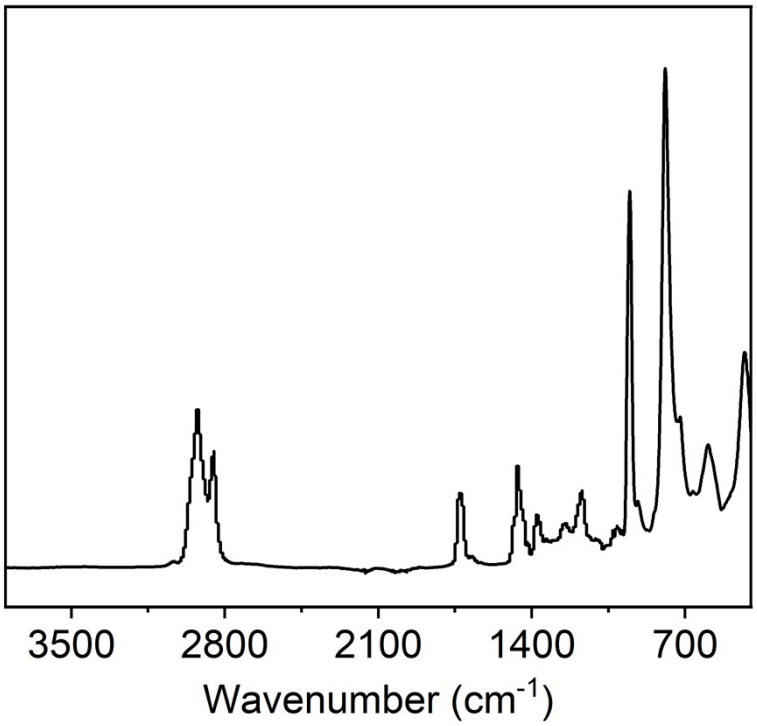

Figure S19. FT-IR spectrum of CSEP after 3 alternating redox cycles in KBr pellet.

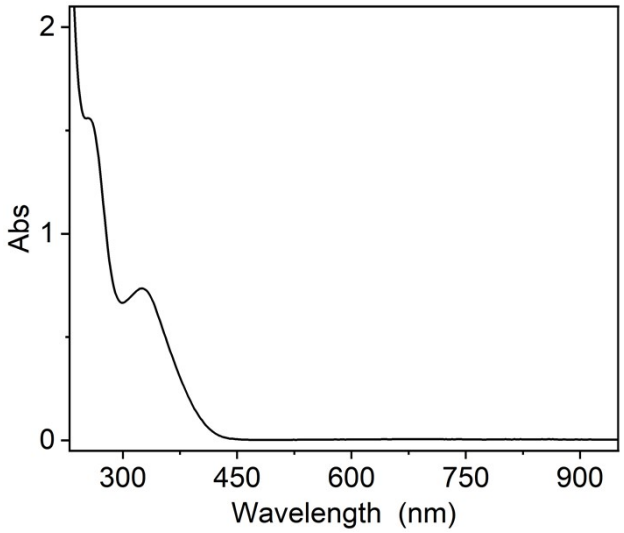

Figure S20. UV-Vis spectrum of CSEP in dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) after 3 alternating redox cycles.

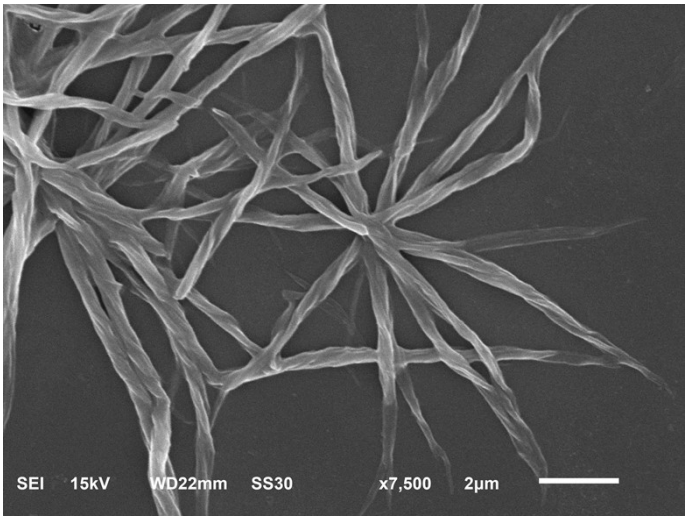

Figure S21. SEM image of CSEP assemblies in dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) solution after the third time H_2O_2 oxidation.

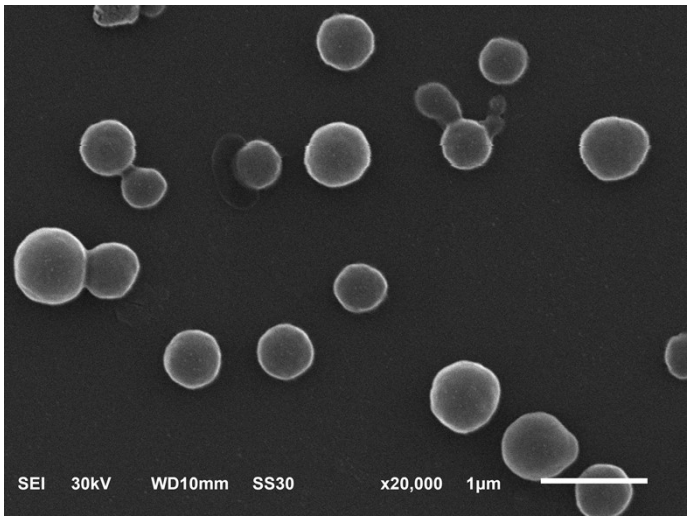

Figure S22. SEM image of CSEP assemblies in dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) solution after the third time UV reduction.

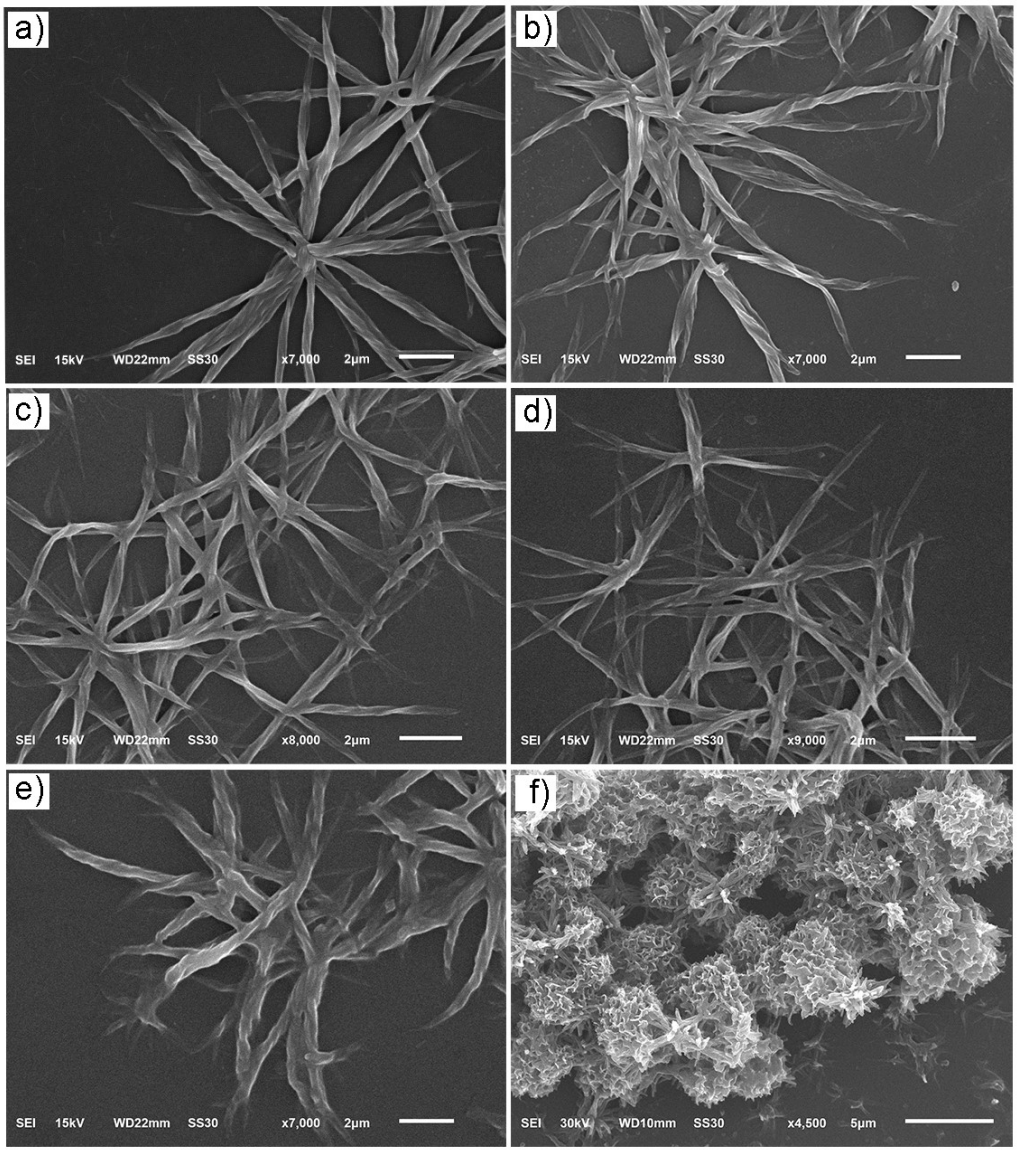

Figure S23. SEM images of CSEP-Py co-assembly systems with different Py doping ratios in dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) solution: a), 5wt%; b), 6wt%; c), 7wt%; d), 9wt%; e), 10wt%; f), 20wt%.

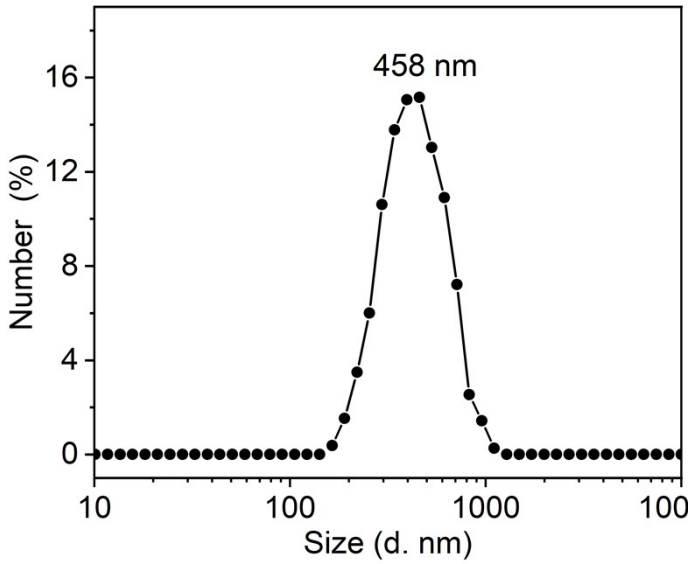

Figure S24. DLS result of CSEP-Py in dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) after UV irradiation for 10 min.

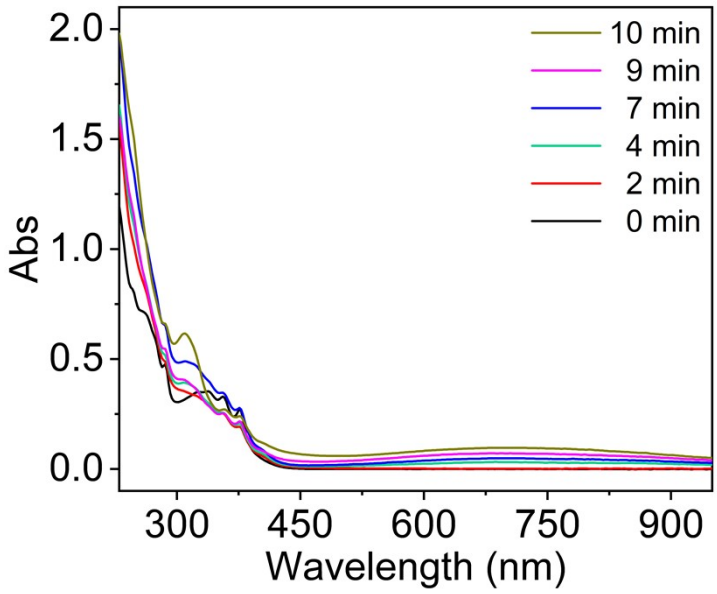

Figure S25. UV-vis spectra of CSEP-Py in dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) under different UV irradiation times.

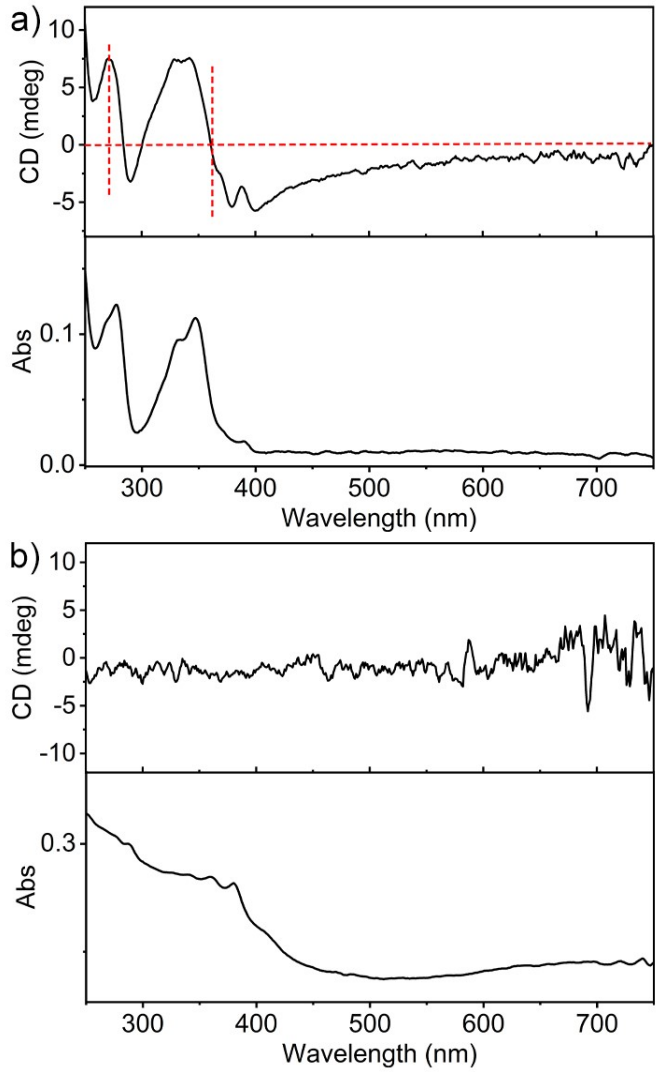

Figure S26. a) CD spectrum of CSEP-Py casting film on quartz substrate obtained from the mixed solvents. b). CD spectra of CSEP-Py casting film on quartz substrate obtained from mixed solvents after UV irradiation for 10 min.

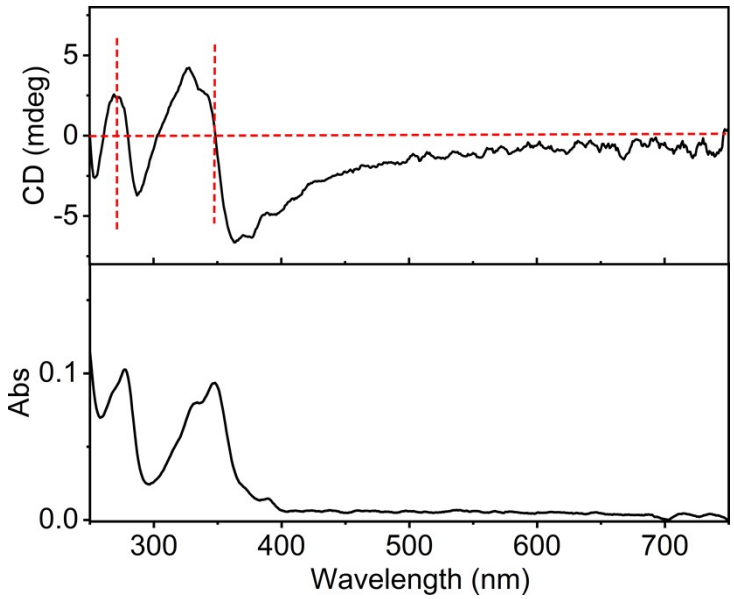

Figure S27. CD spectrum of CSEP-Py casting film on quartz substrate obtained from mixed solvent after treatment with H_2O_2.

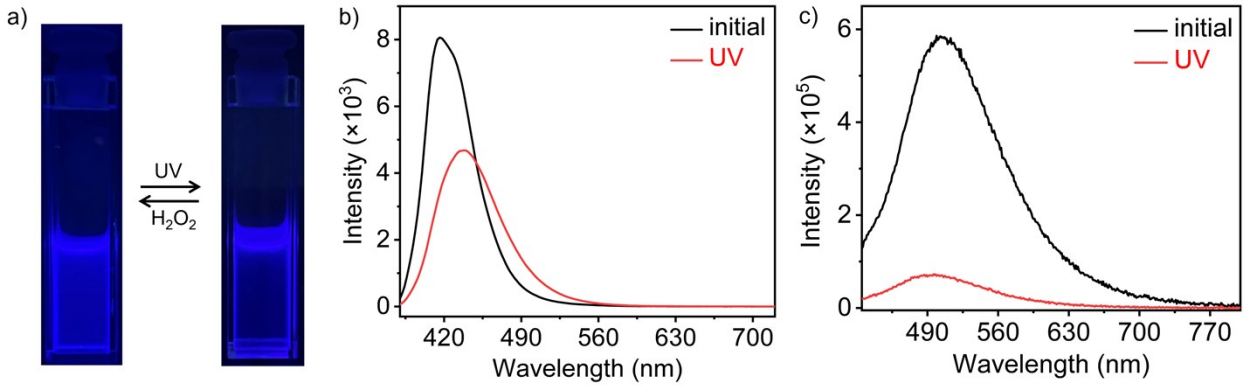

Figure S28. a) Fluorescence photographs before and after UV irradiation. b) Fluorescence spectra of CSEP-Py solution in dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) at the initial state (black line) and after UV irradiation (red line) (λ_{ex} = 360 nm). c) Fluorescence spectra of CSEP-Py sold-film on quartz substrate at the initial state (black line) and after UV irradiation (red line) (λ_{ex} = 360 nm).

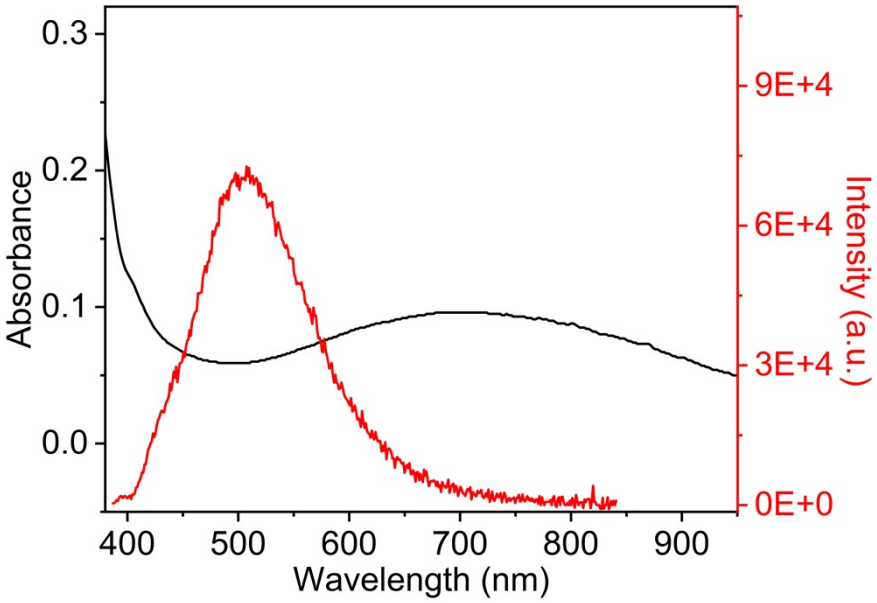

Figure S29. UV-Vis absorption spectrum of CSEP-Py in the mixed solvents of dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) solution at the coloration state after UV irradiation for 10 min and the fluorescence spectrum of CSEP-Py Py solid-film on quartz substrate.

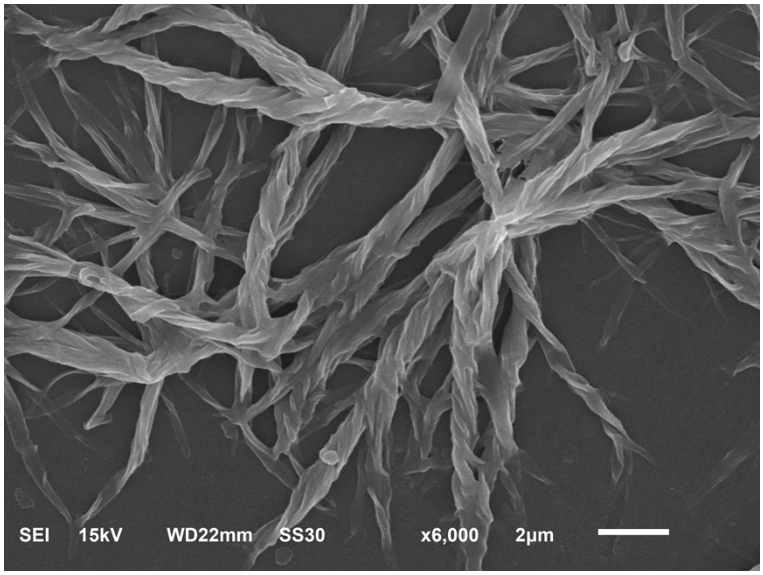

Figure S30. SEM image of CSEP-Py assemblies in the mixed solvents of dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) after the third H_2O_2 oxidation cycle.

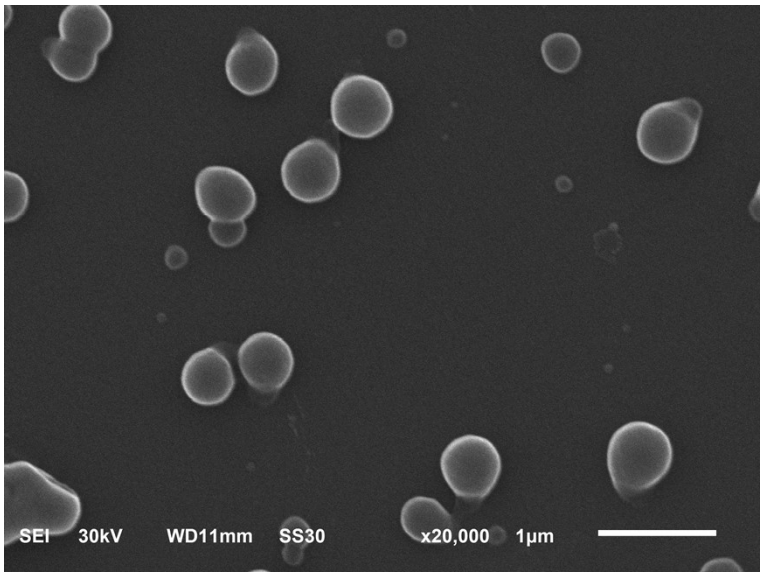

Figure S31. SEM image of spherical assemblies of CSEP-Py obtained from dichloromethane/isopropanol/acetonitrile (10/1/1 v/v/v) after the third time UV light reduction.

Author contributions

J. Zhang proposed the research direction and guided the project. C. Y. Niu designed and performed the experiments and characterization. J. Q. Liu, Q. L. Wu and S. Z, Liu helped with structural characterization. J. J. Tan contributed to the discussion of experimental data. C. Y. Niu and J. Zhang drafted the manuscript. All the authors commented on the manuscript.

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