

Supporting Information for

**Tunable Photo-luminescence Behaviors of Macrocycles
Containing Polymer Networks in Solid-state**

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1. General information.

Solid-state NMR experiments were performed on a Varian instrument at room temperature (25 °C) and at frequencies of 100.52 MHz for ^{13}C . Infrared spectroscopy (IR) was performed on a Thermo Nicolet iS10 with a diamond ATR attachment. Transmission electron microscope (TEM) images were obtained on a Tecnai G2 F20 microscope (FEI) with an accelerating voltage of 200 kV. The samples were prepared by placing a drop of solution onto a carbon-coated copper grid and air-dried. Scanning electron microscopy (SEM) images were obtained using a JSM-7500F scanning electron microscope. Surface area measurements were conducted on a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer. Each sample (50 mg) was degassed at 100 °C for 24 h and then backfilled with N_2 . Surface parameters were determined using BET adsorption models included in the instrument software (Micromeritics ASAP 2020 V4.00). The samples were prepared by placing a drop of solution onto a coverslip and air-dried. UV/vis spectra were recorded in a quartz cell (light path 5 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. Solid-state fluorescence emission spectra, quantum yields and fluorescence decay profiles were measured on a FLS 920P fluorescence spectroscopy. Thermal gravimetric analysis (TGA) were measured by using a NETZSCH TG209 under N_2 (15ml/min) atmosphere in the range of 20 °C and 800 °C at rate of 10 K/min.

2. Synthesis of TPE polymers.

Synthesis of TPECD polymer: Under argon atmosphere, to a 10 mL thick-walled pressure tube reactor, the mixed solution of 4.5 ml THF and 0.5 ml DMF, 4*p*-bromomethyl-TPE (180 mg, 0.257 mmol), β -CD (100 mg, 0.090 mmol) and K_2CO_3 (160 mg, 1.16 mmol) was added. The mixture was kept at 80 °C for 2 days, then a light yellow solid was obtained by centrifuged. The excessive K_2CO_3 was removed by washing the solid with 1 M HCl until CO_2 evolution stopped. The recovered solid was isolated and activated under ultrasonic bath in H_2O (2×10 ml), THF (2×10 ml) and CH_2Cl_2 (1×10 ml) for 15 min each. Finally, the TPECD polymer was gained through lyophilized. ^{13}C -CPMAS NMR (100 MHz): δ 26.2, 51.2, 68.5, 131.9, 142.1 ppm. IR (solid, attenuated total reflectance, ATR): 3411, 3025, 2926, 1685, 1603, 1565, 1510, 1458, 1412, 1367, 1261, 1212, 1154, 1083, 1036, 846, 793, 575, 503 cm^{-1} . Elemental analysis: C 48.12 %, H 5.03 %.

Synthesis of pTPESC4A polymer: Under argon atmosphere, to a 10 mL thick-walled pressure tube reactor, the mixed solution of 4.5 ml THF and 0.5 ml DMF, 4*p*-bromomethyl-TPE (100 mg, 0.142 mmol), SC4A (118 mg, 0.142 mmol) and K_2CO_3 (94 mg, 1.16 mmol) was added. The mixture was kept at 80 °C for 2 days, then a light yellow solid was obtained by centrifuged. The excessive K_2CO_3 was removed by washing the solid with 1 M HCl until CO_2 evolution stopped. Then 1 M NaOH was added to pH = 10 to regain the sodium sulfonate. The recovered solid was isolated and activated under ultrasonic bath in H_2O (2×10 ml), THF (2×10 ml) and CH_2Cl_2

(1 × 10 ml) for 15 min each. Then redistribute it into water, and took the supernatant after centrifugation to subject to UV-Vis spectroscopy to ensure no free SC4A. If there exist substrates, repeat the washing procedure(Figure S3). Finally, the pTPESC4A polymer was gained through lyophilized. ¹³C-CPMAS NMR (100 MHz): δ 22.4, 32.7, 47.2, 51.1, 65.1, 70.5, 131.6 and 141.6 ppm. IR (solid, attenuated total reflectance, ATR): 3416, 3026, 2924, 2867, 1742, 1690, 1662, 1600, 1566, 1510, 1476, 1413, 1388, 1268, 1210, 1179, 1183, 1043, 1017, 874, 820, 795, 742, 660, 629 and 561 cm⁻¹. Elemental analysis: C 48.35 %, H 3.05 %.

3. Basic characterizations of the crosslinked polymers.

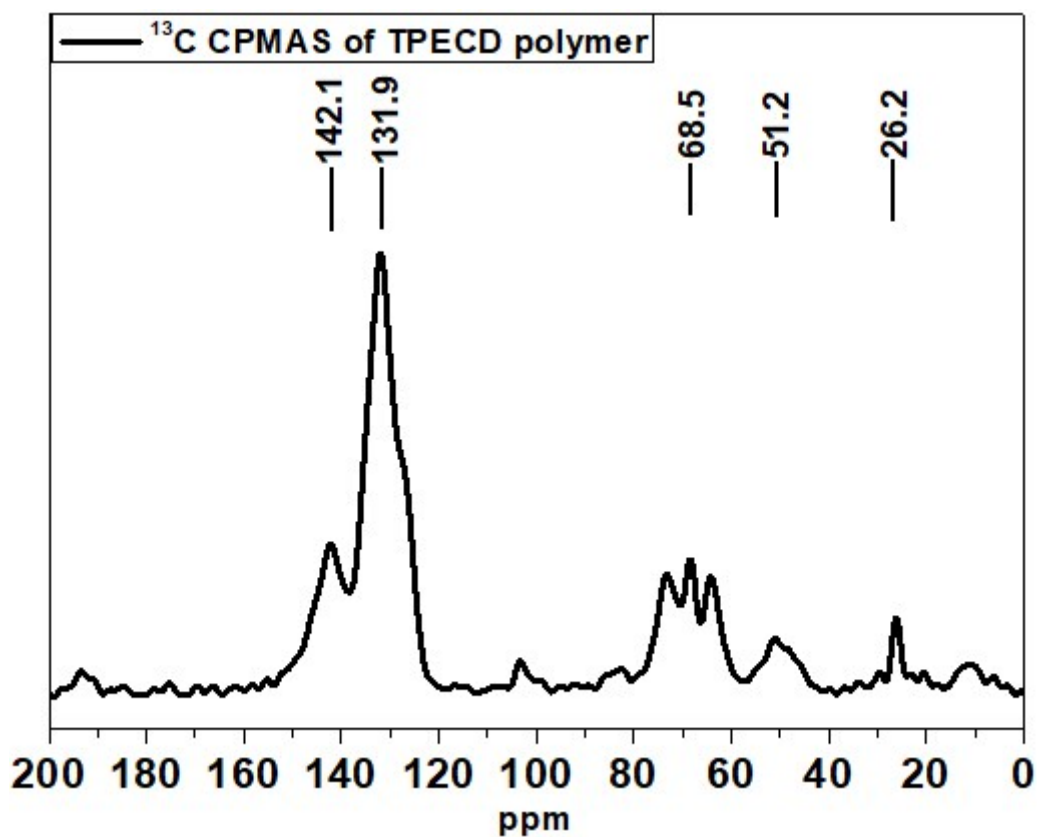


Figure S1. Solid-state ¹³C NMR of TPECD polymer.

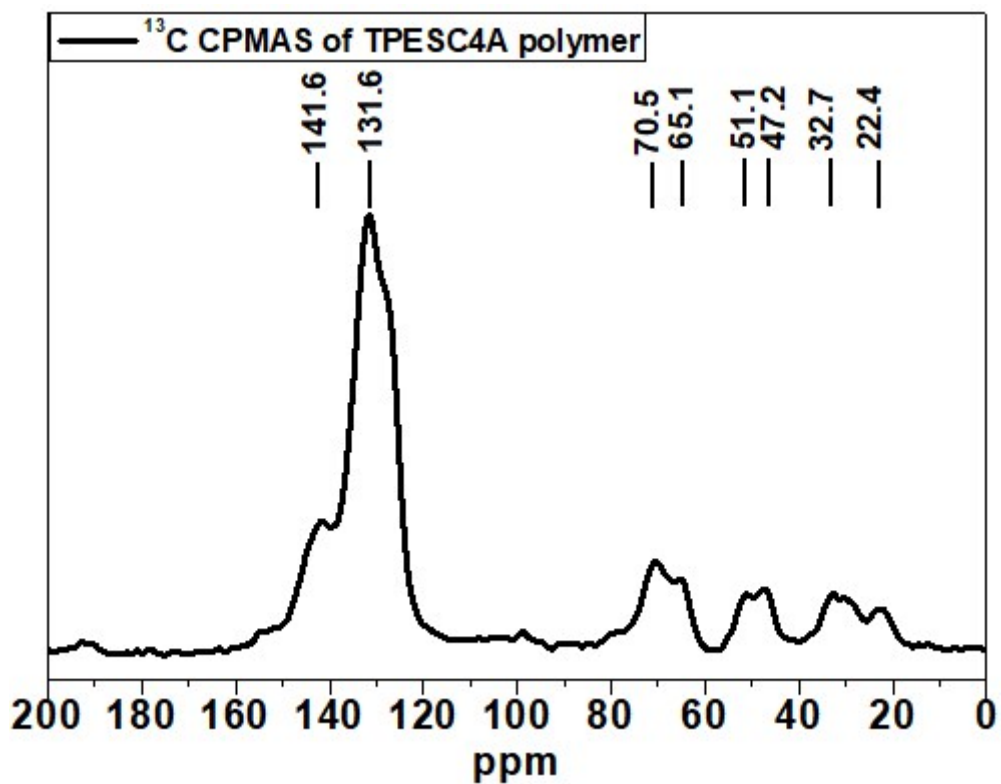


Figure S2. Solid-state ¹³C NMR of TPESC4A polymer.

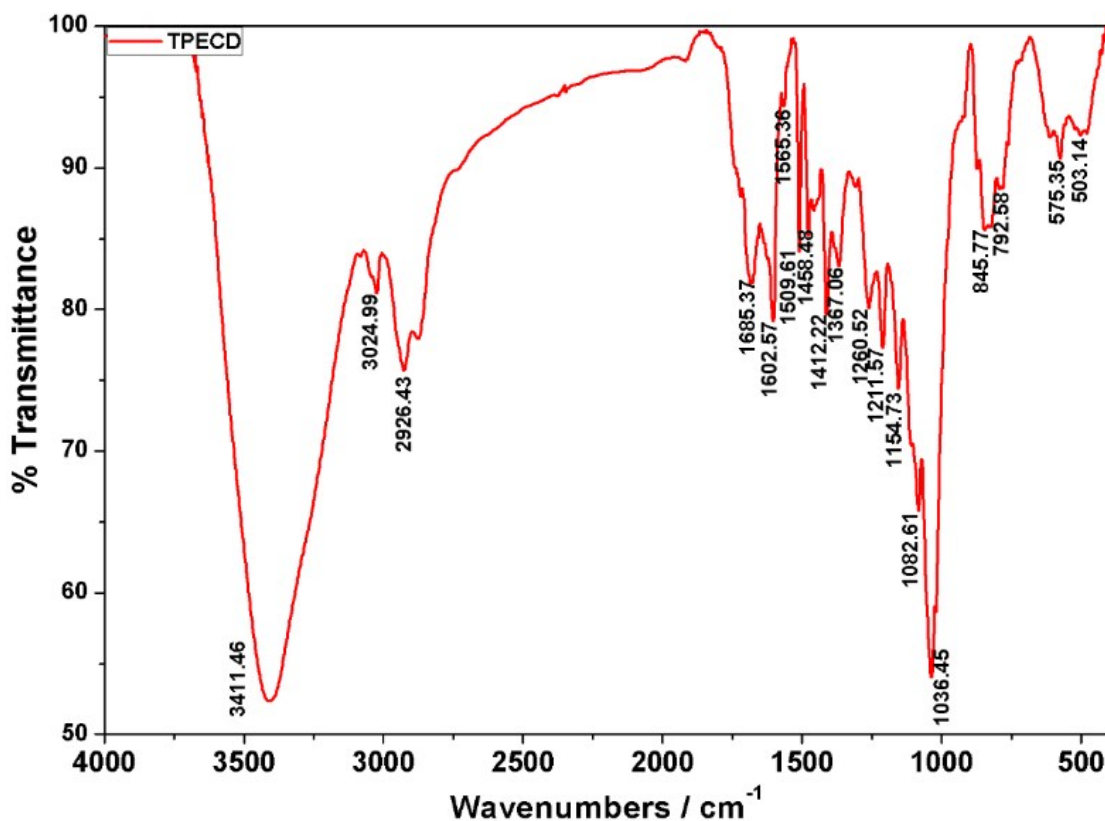


Figure S3. FT-IR of TPECD polymer. Peaks at 1602.57, 1565.36, 1509.61 and 1458.48 cm^{-1} with different intensities were attributed to aromatic C=C frame vibration, and the peaks at 845.77 and 792.58 cm^{-1} were corresponded to the aromatic C-H bending vibration, which jointly demonstrated the appearance of TPE unit. The spectrum also exhibited O-H stretch at 3411.46 cm^{-1} , aliphatic C-H stretches around 2926.43 cm^{-1} , and an intense C-O stretch at 1036.45 cm^{-1} , which are the typical spectral features of intact β -CD.

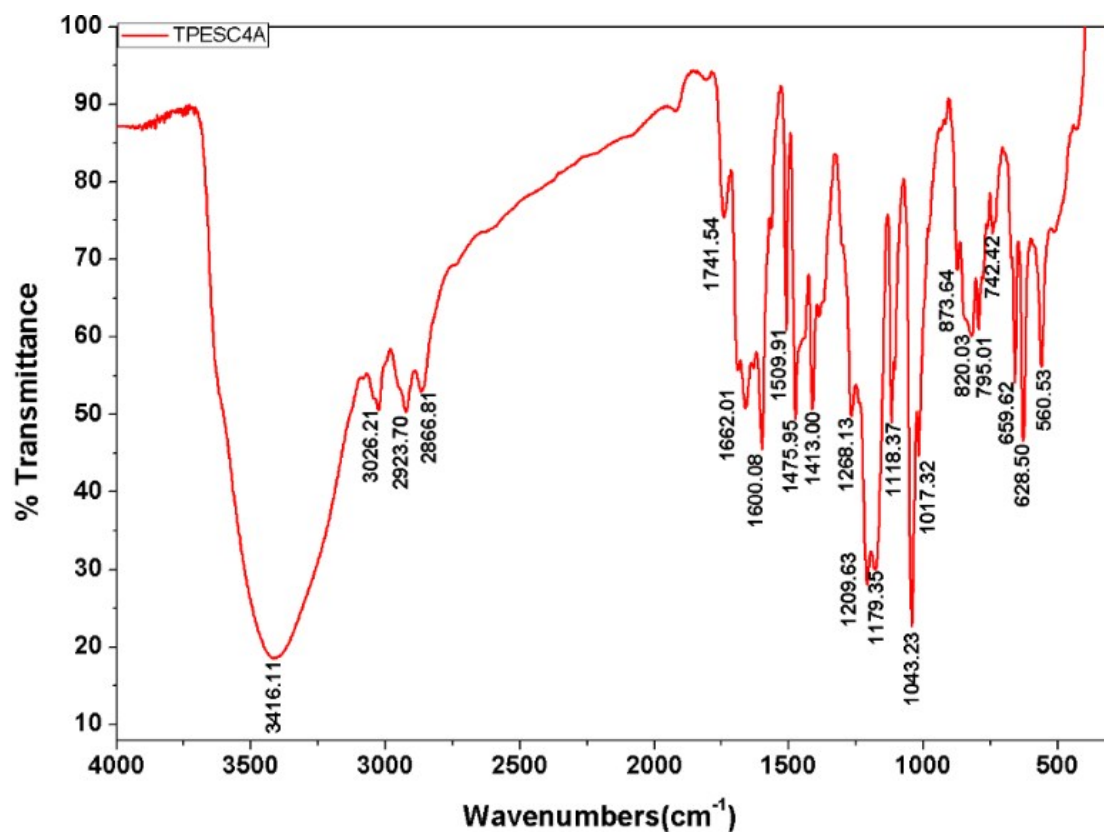


Figure S4. FT-IR of TPESC4A polymer.

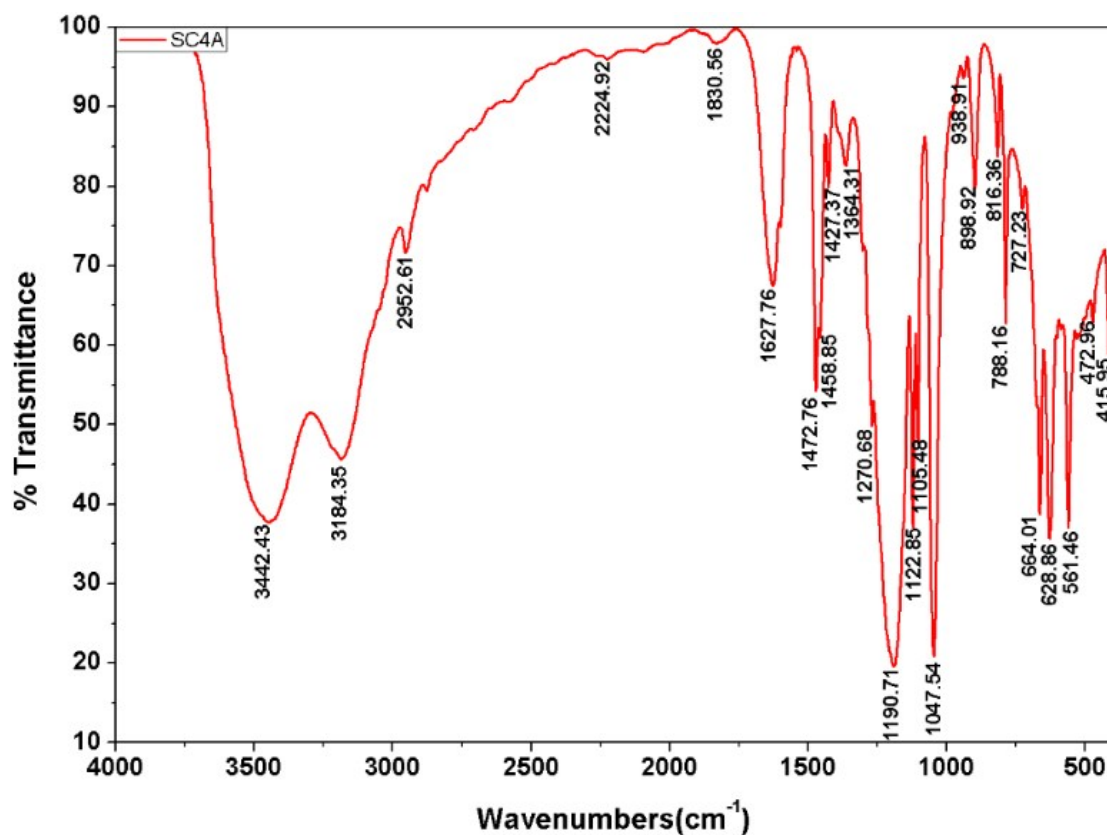


Figure S5. FT-IR of SC4A.

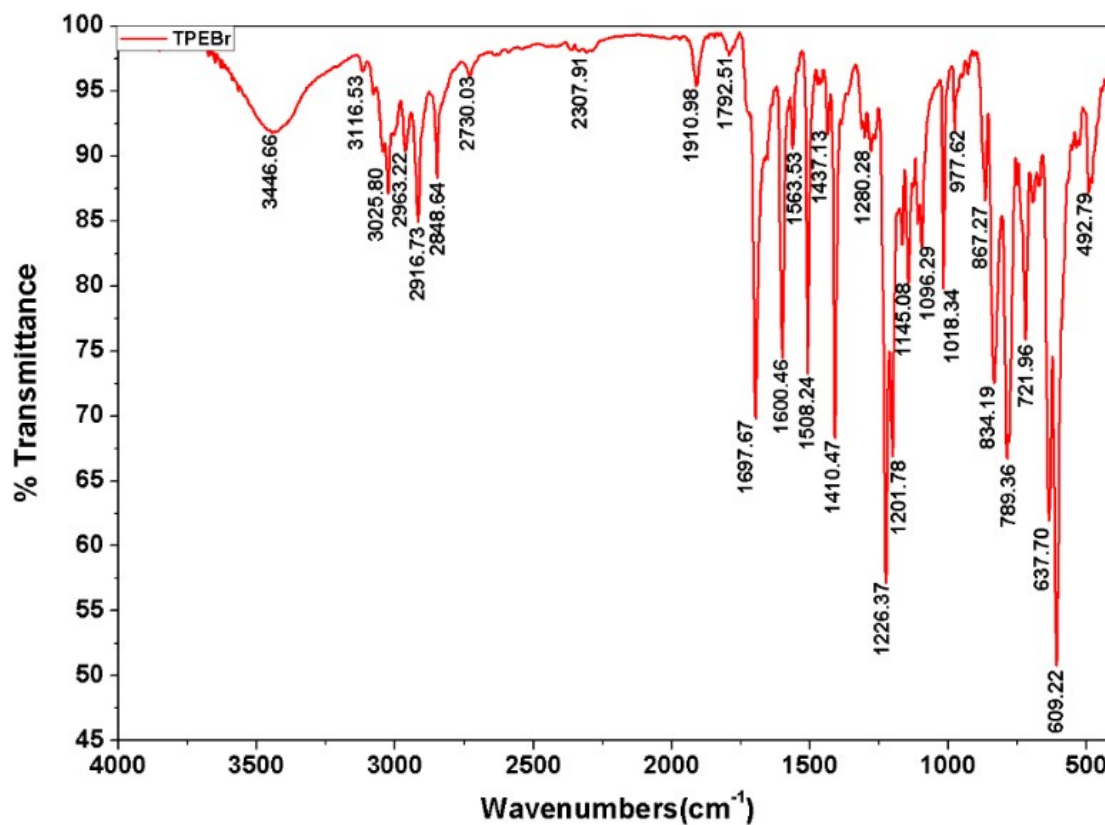


Figure S6. FT-IR of TPEBr. Comparing the FT-IR spectrum of SC4A and TPESC4A (Figure S4-S6), the strong broaden peak at 3184.35 cm⁻¹ relating to the intramolecular hydrogen bonding of SC4A was disappeared in TPESC4A, and the intense peaks at 1017.32 (aliphatic C-O), 1179.35, 1209.63 cm⁻¹ (aromatic C-O) in TPESC4A suggested the ether (Ar-O-R) formation, Also comparing with SC4A, the split of C-S (1040-1050 cm⁻¹) and aromatic C-O (1190.71 cm⁻¹) indicated the incomplete crosslinking of all hydroxy of SC4A.

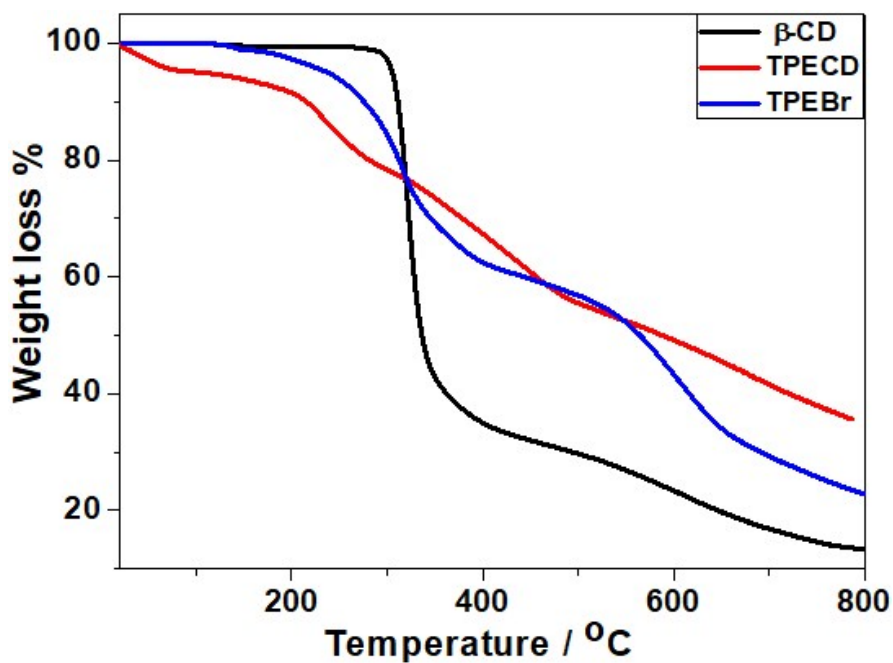


Figure S7. TG spectra of β -CD (black), TPECD polymer (red) and TPEBr (blue).

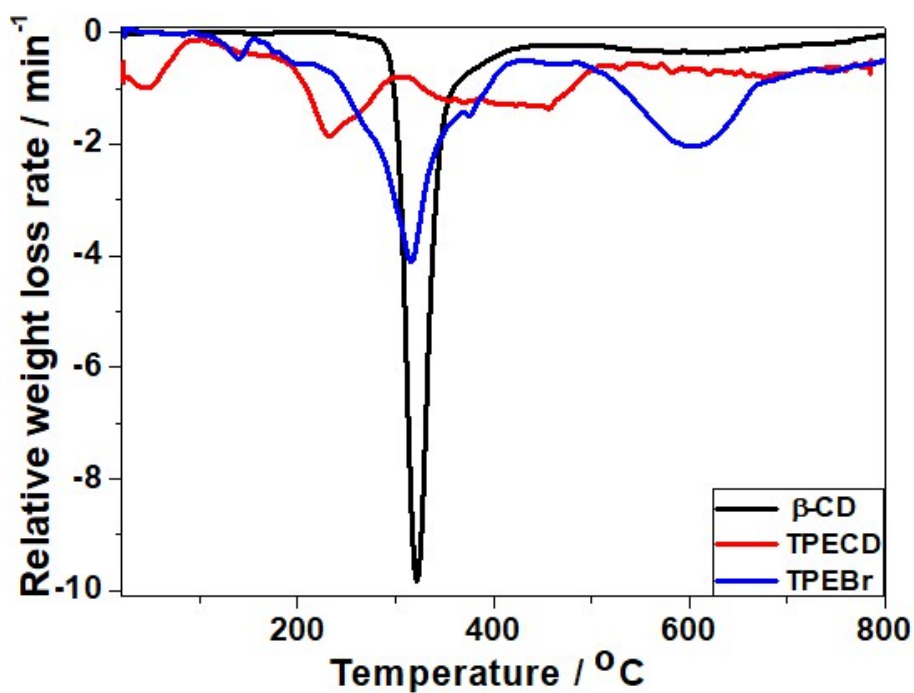


Figure S8. DTG spectra of β -CD (black), TPECD polymer (red) and TPEBr (blue). TPECD polymer fall down sharply in about 230 °C, suggesting its easy degradation.

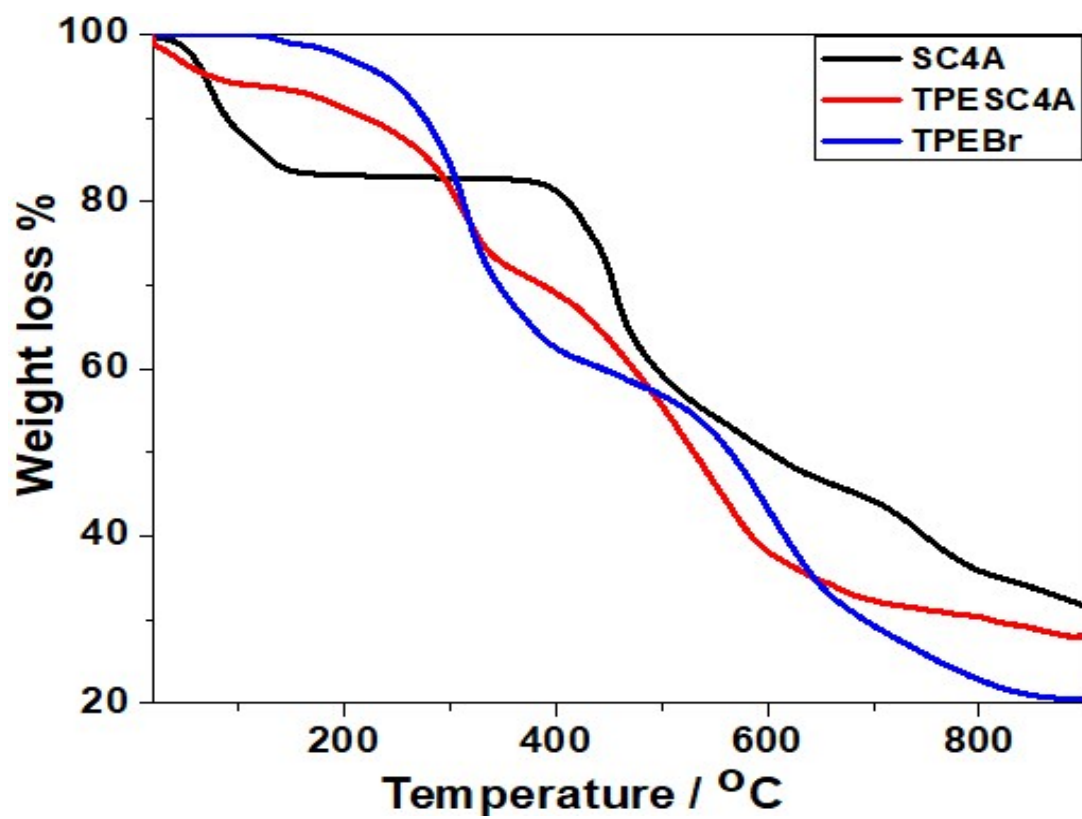


Figure S9. TG spectra of SC4A (black), pTPESC4A polymer (red) and TPEBr (blue).

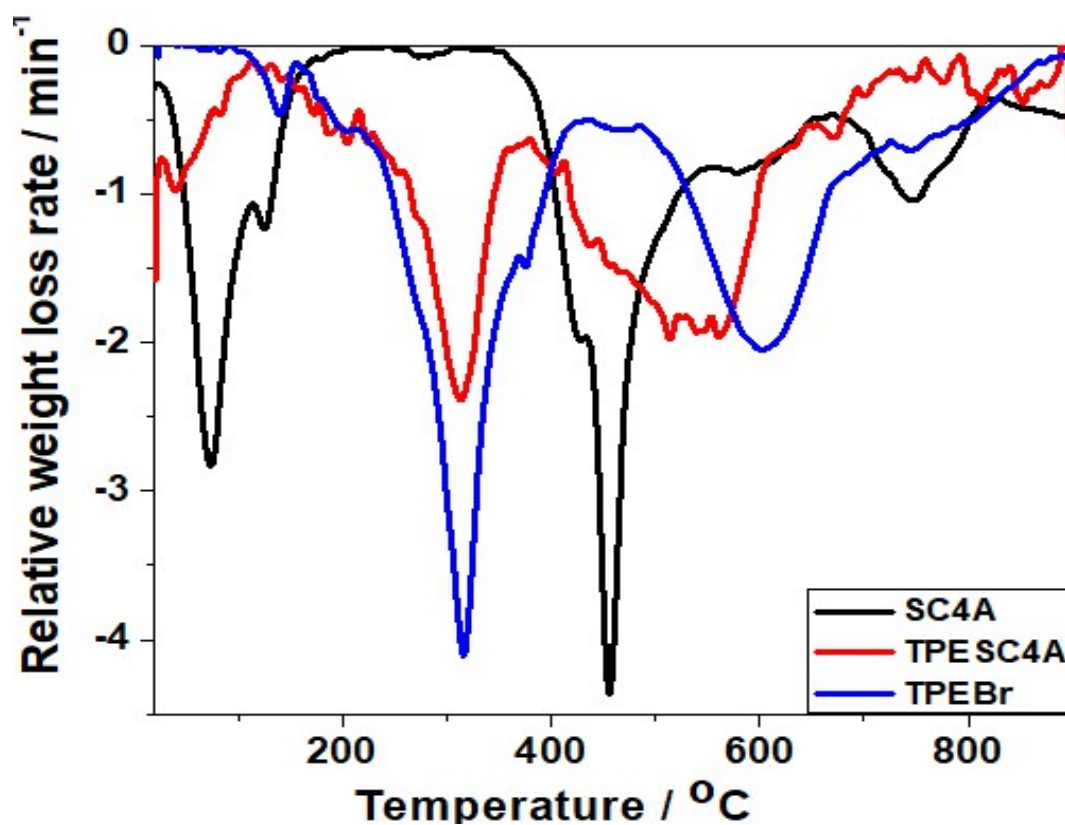


Figure S10. DTG spectra of SC4A (black), pTPESC4A polymer (red) and TPEBr (blue). TPEBr as well as TPESC4A gave a most acute peak at 310 °C suggesting that the polymer maintained its precursors' thermal stability in this temperature range. While between 490-640 °C, TPESC4A curve fell below its parents'(TG) and combined the two peaks at 460 °C and 610 °C to a wide peak at 510-570 °C(DTG) indicating that a covalent connection between TPEBr and SC4A rather than simple physical mixing.

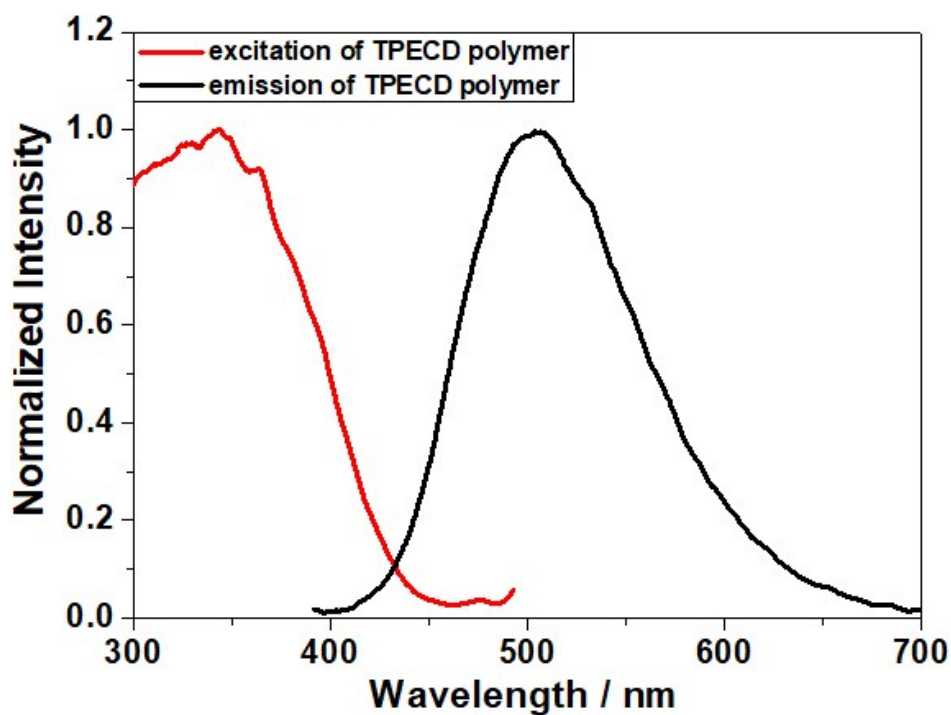


Figure S11. Normalized solid FL excitation (em: 500 nm, red) and emission spectra (ex: 360 nm, black) of TPECD polymer.

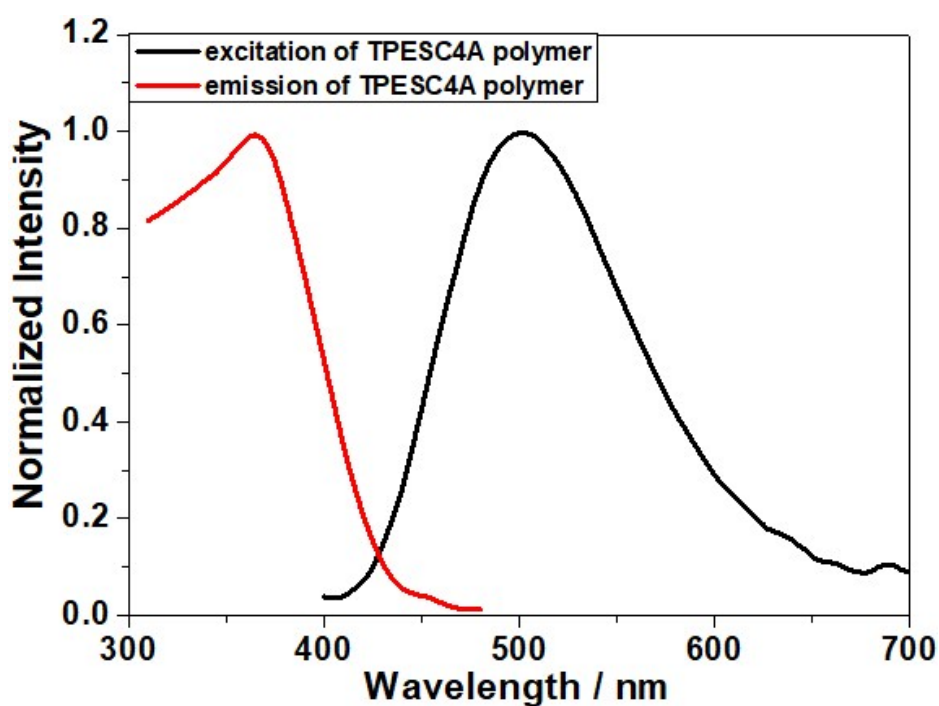


Figure S12. Normalized solid FL excitation (em: 500 nm, red) and emission spectra (ex: 365 nm, black) of TPESC4A polymer.

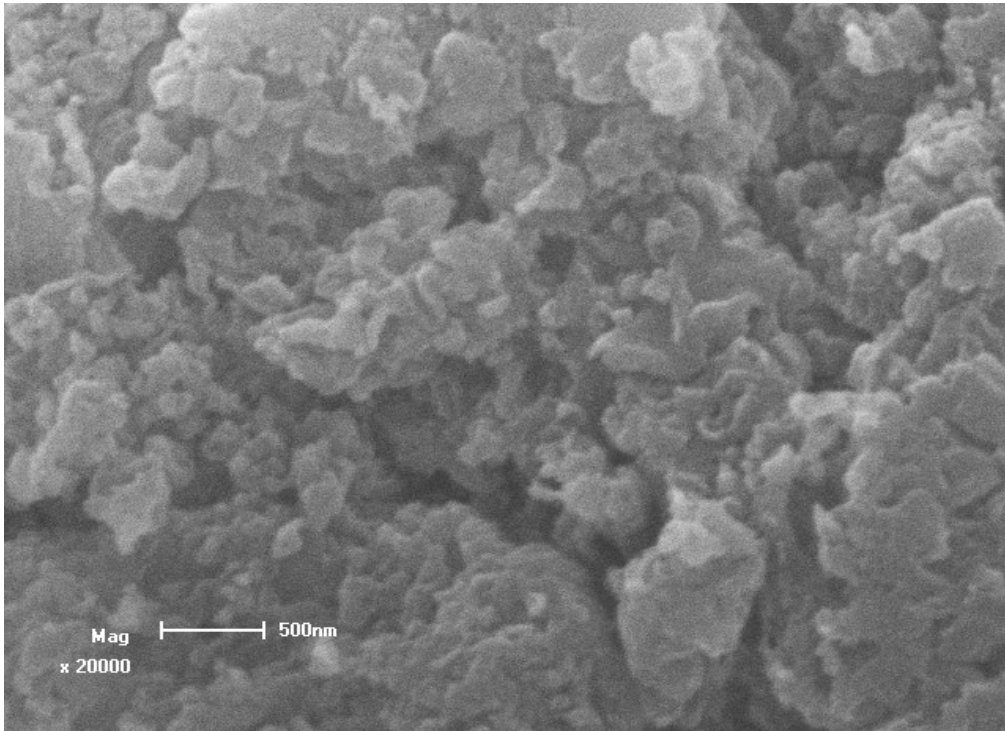


Figure S13. SEM image of TPECD polymer.

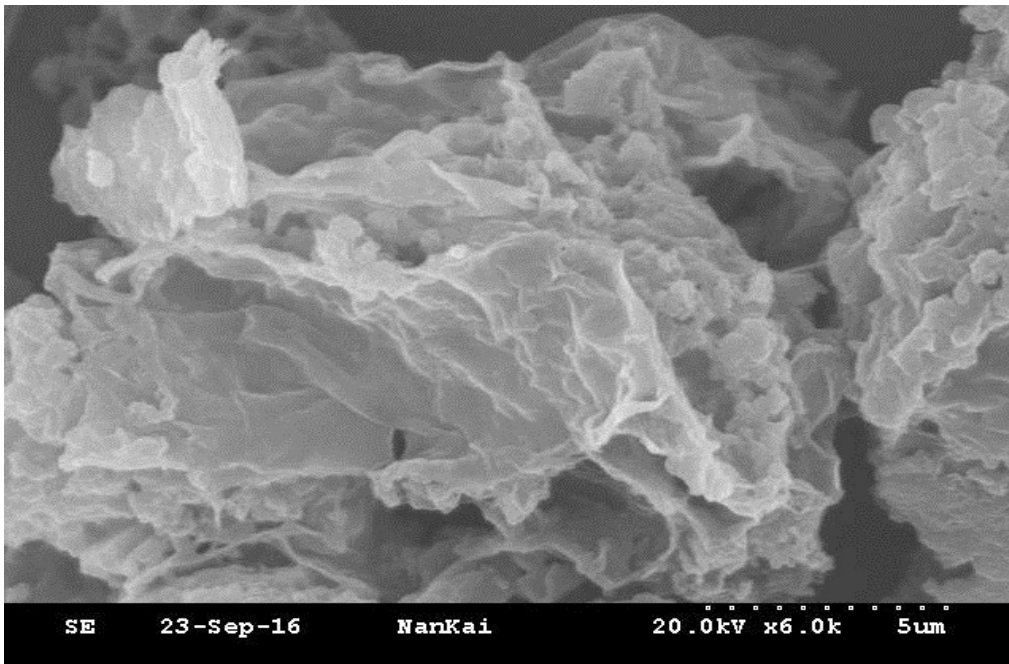


Figure S14. SEM image of TPESC4A polymer.

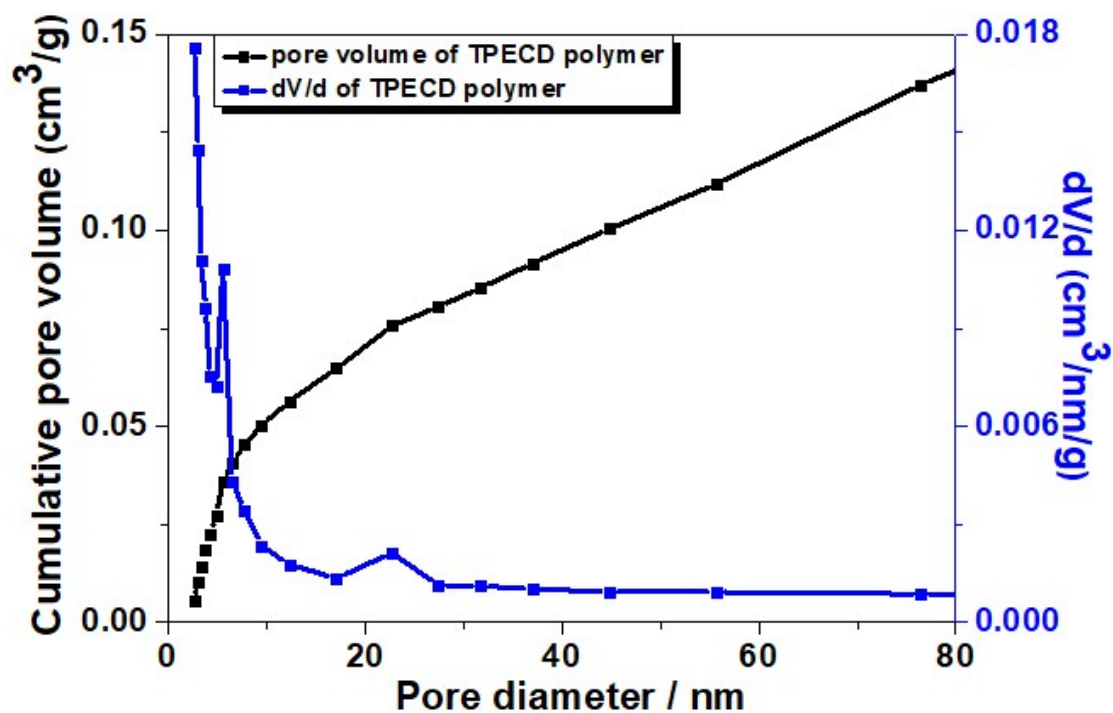


Figure S15. The cumulative pore volume (black) and distribution of surface area (blue) along with pore diameter of TPECD polymer obtained by BJH analysis.

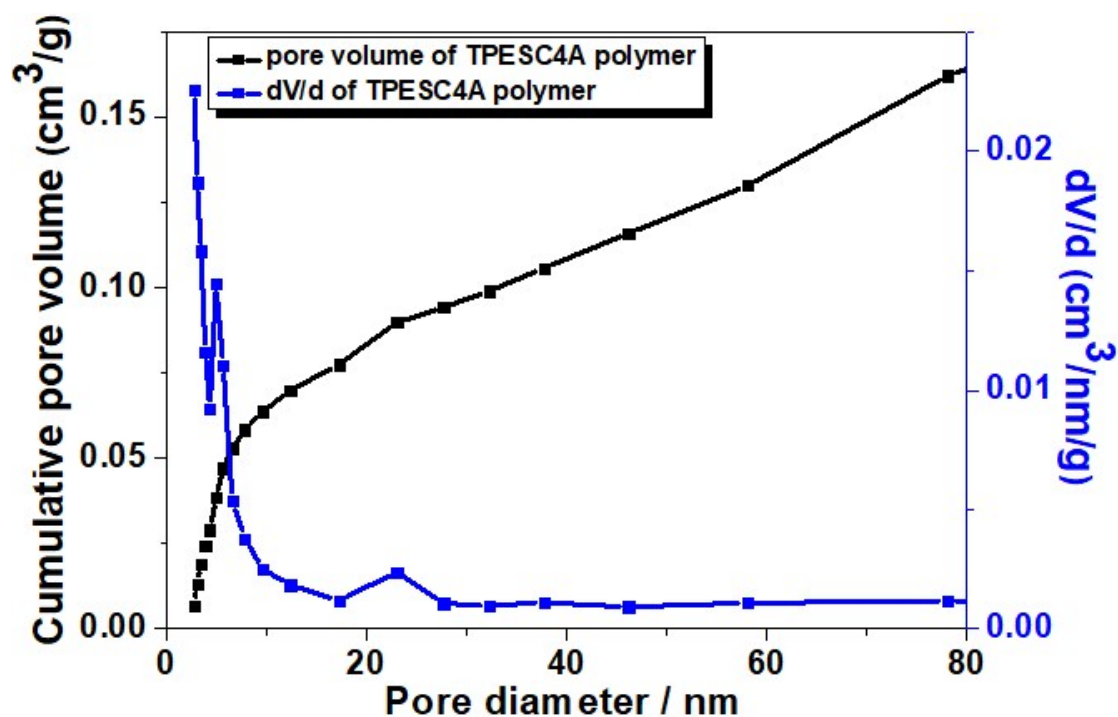


Figure S16. The cumulative pore volume (black) and distribution of surface area (blue) along with pore diameter of TPESC4A polymer obtained by BJH analysis.

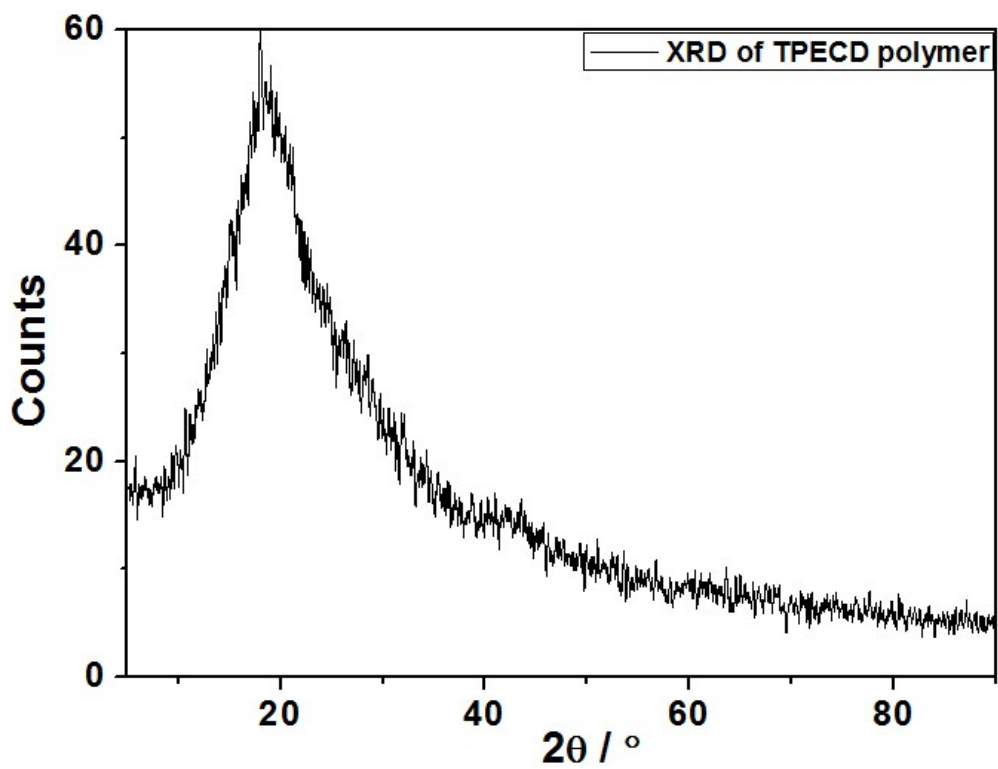


Figure S17. XRD of TPECD polymer (5-90°).

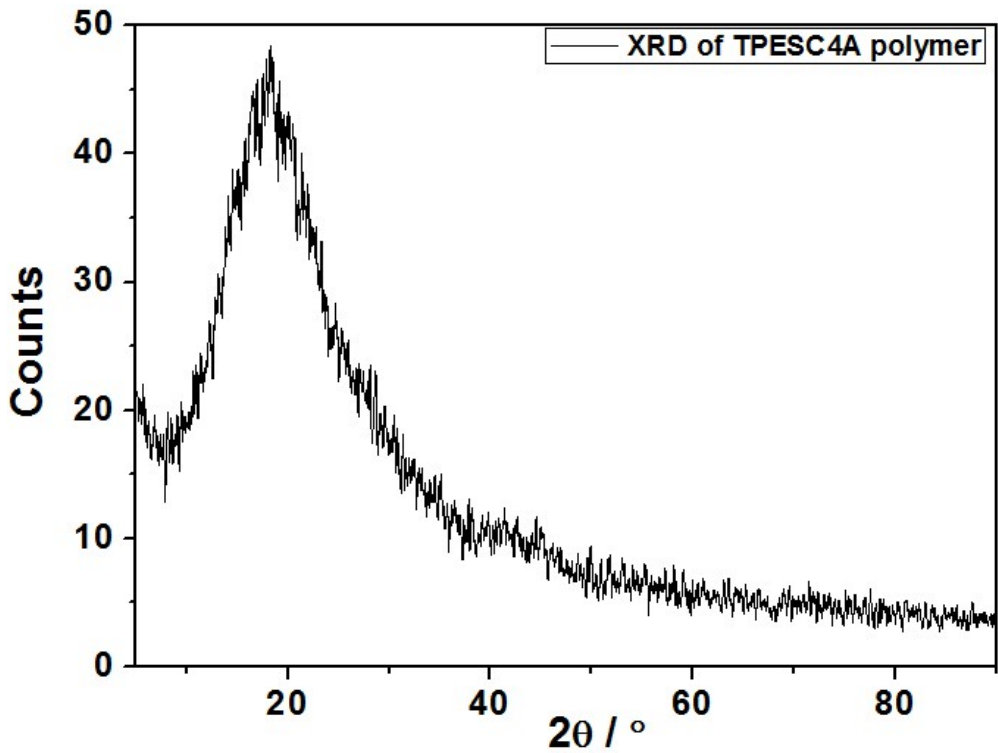


Figure S18. XRD of TPESC4A polymer (5-90°).

4. Adsorption capability of TPECD and TPESC4A polymers.

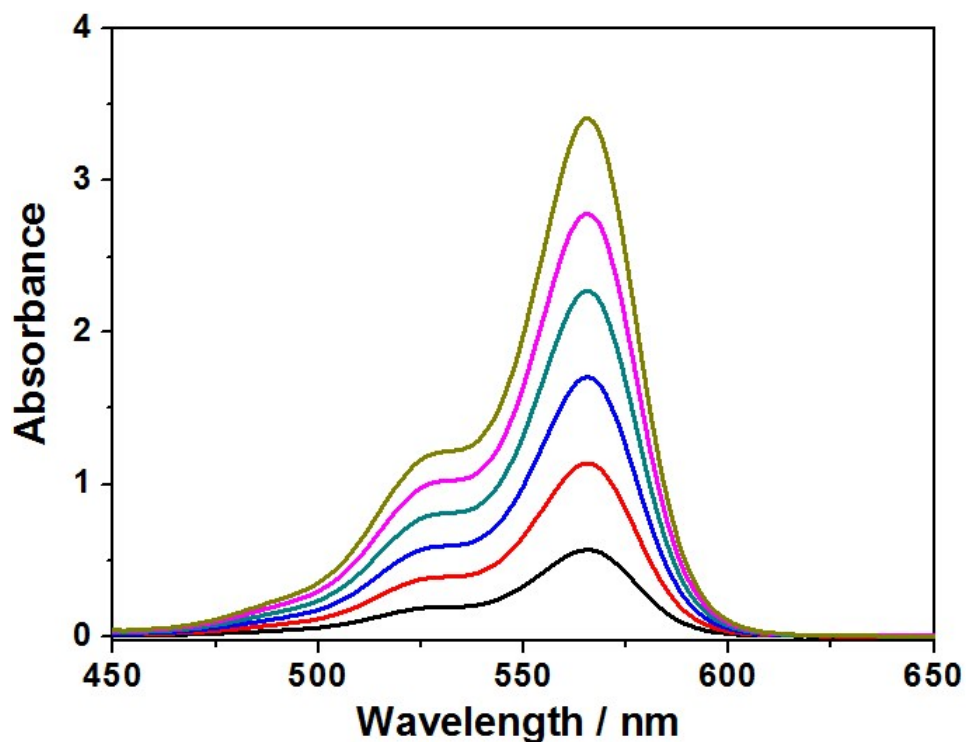


Figure S19. UV-Vis spectra of a series of concentrations (10, 20, 30, 40, 50, 60 μmol/L) of sRhB.

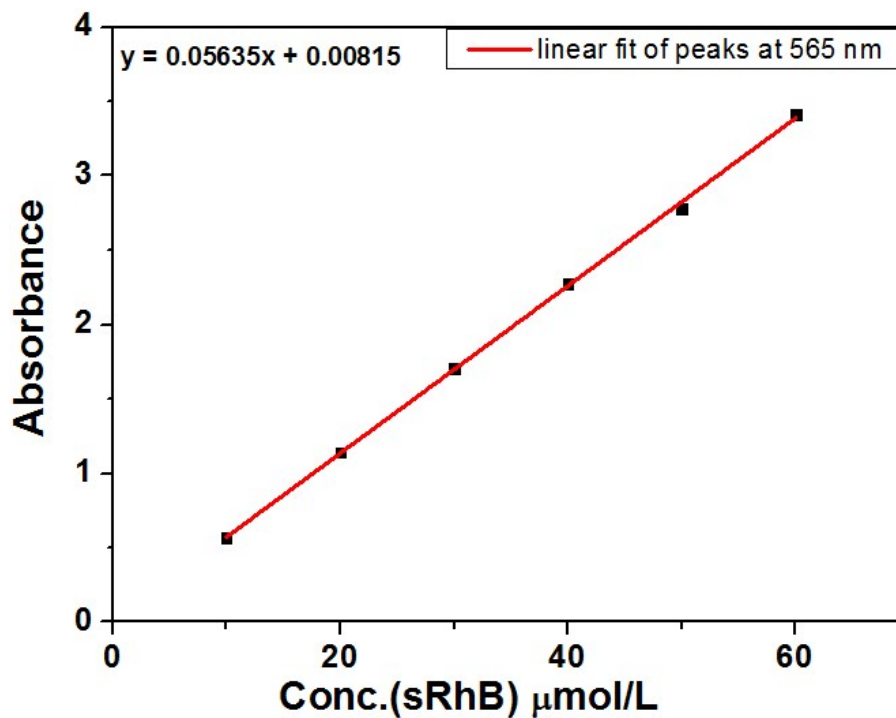


Figure S20. Linear fitting of UV-Vis absorbance of sRhB at 565 nm.

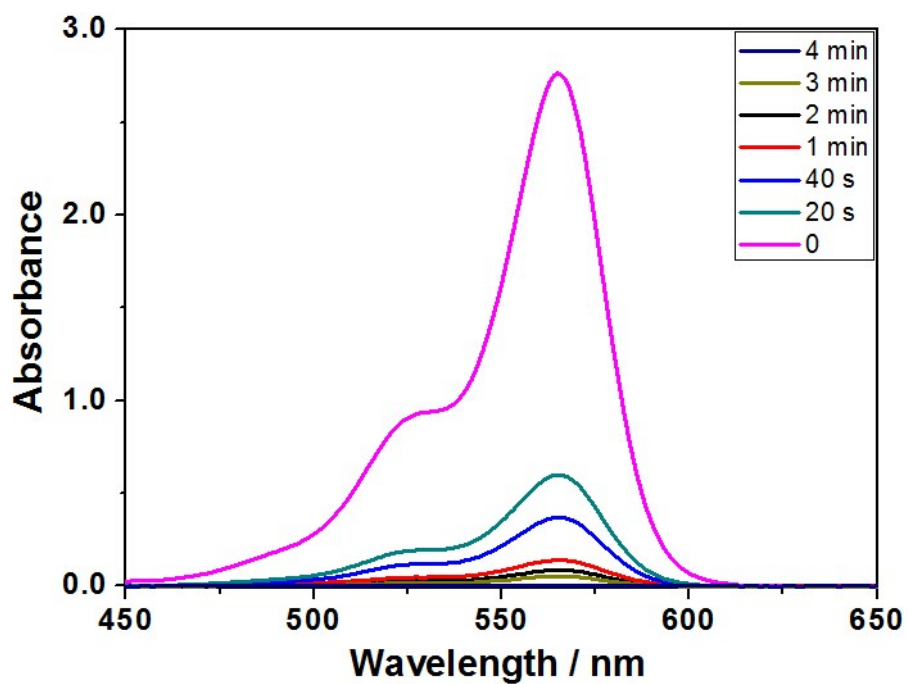


Figure S21. UV-Vis spectra of sRhB (50 $\mu\text{mol/L}$) after adsorbed by TPECD polymer for a certain time (0, 20s, 40s, 1 min, 2 min, 3 min, 4 min).

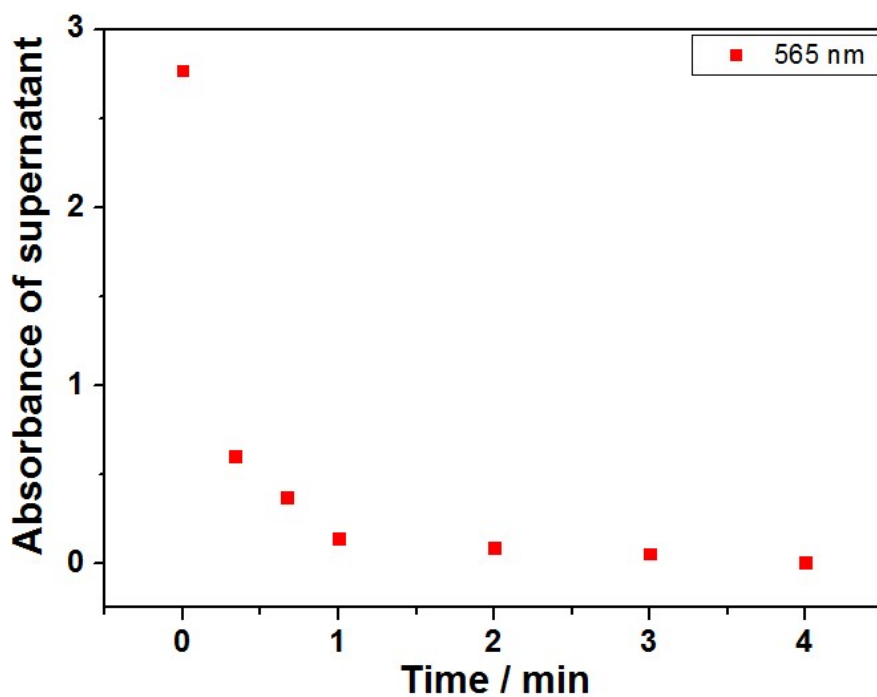


Figure S22. Changes of UV-Vis absorbance of sRhB at 565 nm (50 $\mu\text{mol/L}$) along with the time (0, 20s, 40s, 1 min, 2 min, 3 min, 4 min).

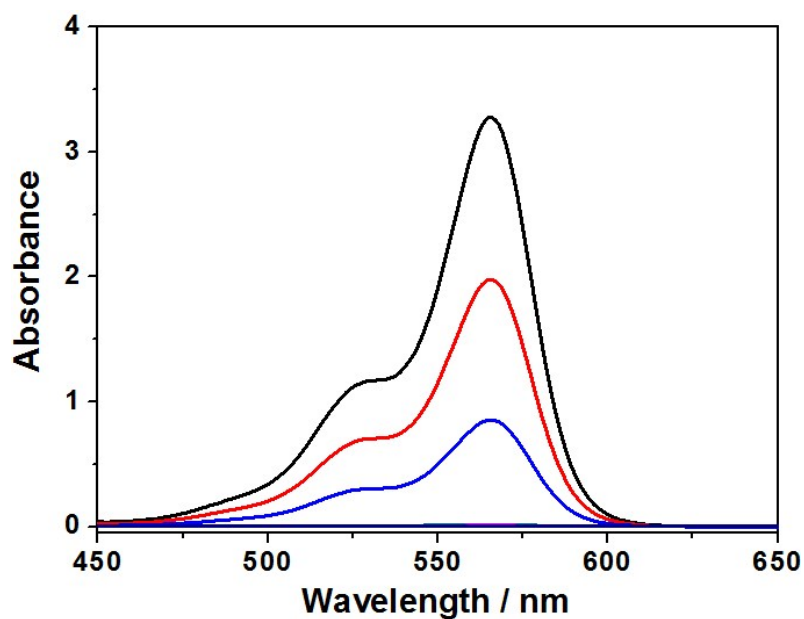


Figure S23. UV-Vis spectra of sRhB supernatant after adsorbed by TPECD polymer (1 mg polymer for 1 mL dye solution) (concentrations before absorbed are 5, 10, 25, 50, 75, 100, 125 $\mu\text{mol/L}$ from bottom up.

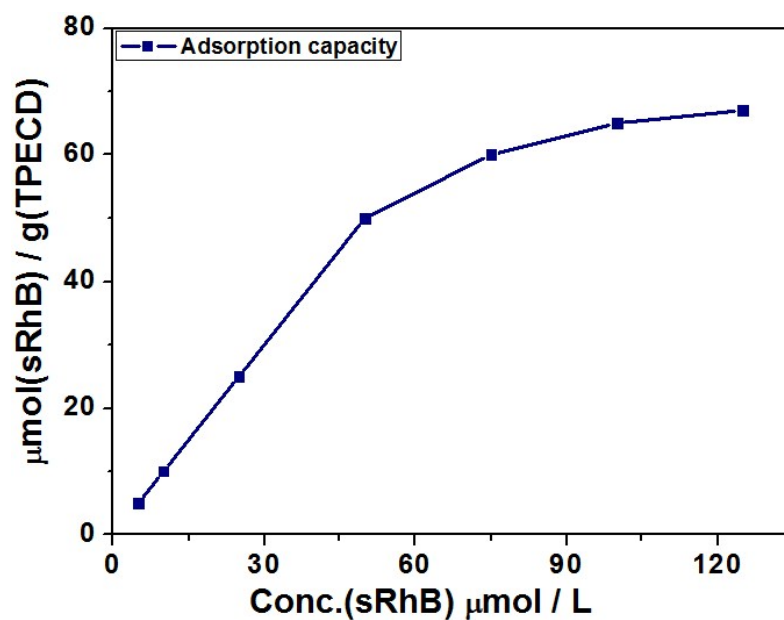


Figure S24. Adsorbed amount of sRhB along with the increase concentrations of sRhB calculated from the UV-Vis absorbance work plot.

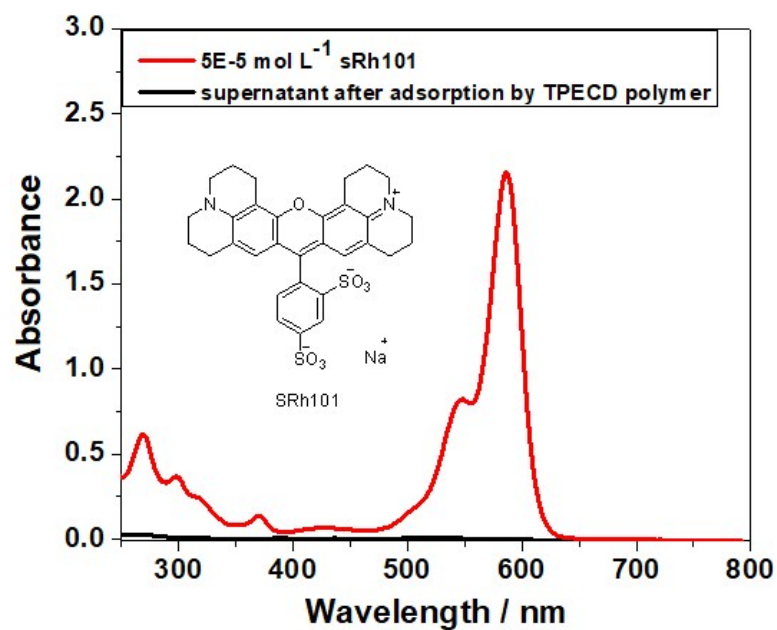


Figure S25. UV-Vis absorbance of sRh101 (50 μM , red) and supernatant after adsorption by TPECD polymer (1 mg mL⁻¹, black) (1 mg polymer with 1 mL 50 μM dye solution for 5 minutes).

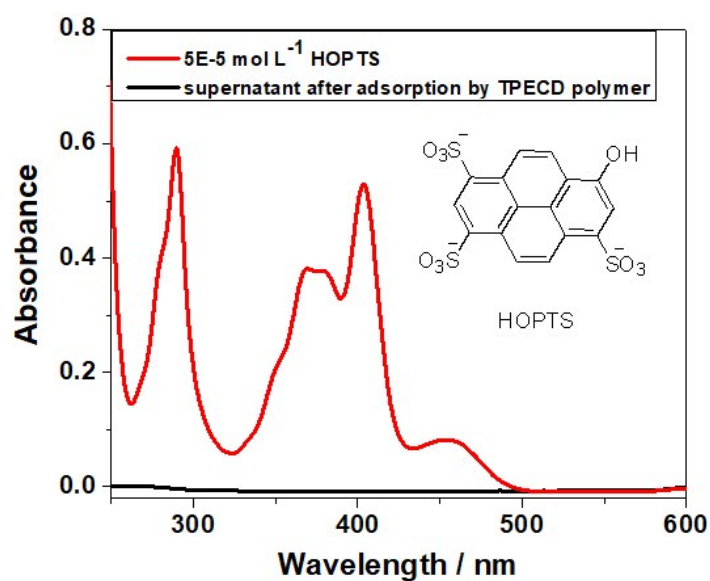


Figure S26. UV-Vis absorbance of HOPTS (50 μM , red) and supernatant after adsorption by TPECD polymer (1 mg mL⁻¹, black) (1 mg polymer with 1 mL 50 μM dye solution for 5 minutes).

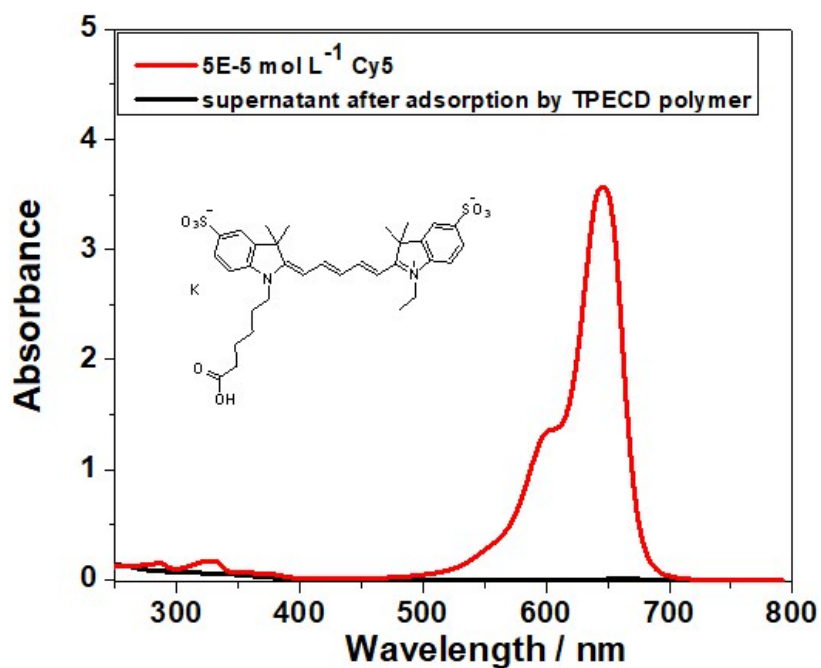


Figure S27. UV-Vis absorbance of Cy5 (50 μM , red) and supernatant after adsorption by TPECD polymer (1 mg mL⁻¹, black) (1 mg polymer with 1 mL 50 μM dye solution for 5 minutes).

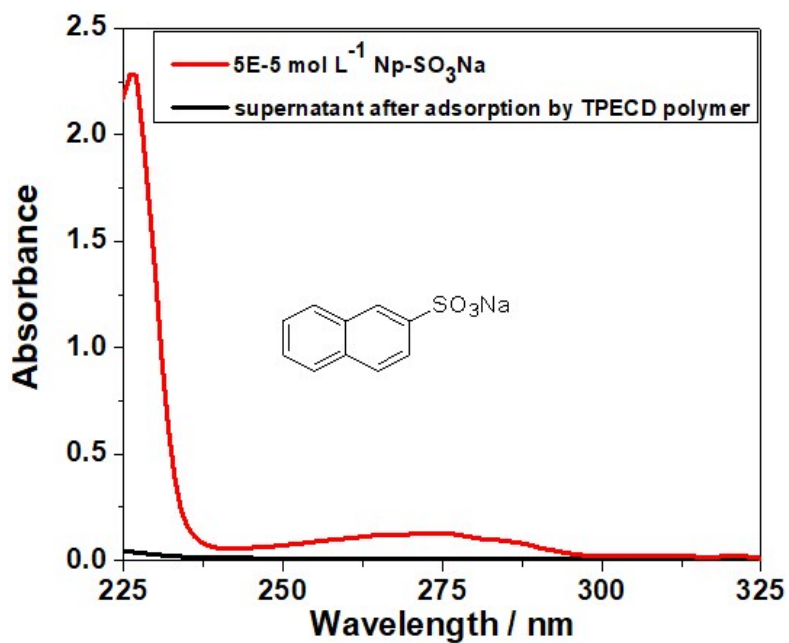


Figure S28. UV-Vis absorbance of Np-SO₃Na (50 μM , red) and supernatant after adsorption by TPECD polymer (1 mg mL⁻¹, black) (1 mg polymer with 1 mL 50 μM dye solution for 5 minutes).

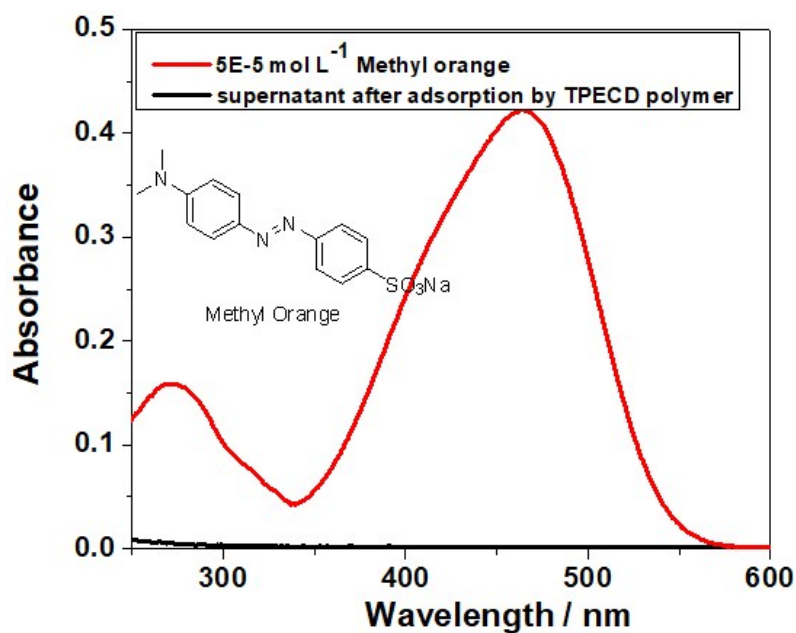


Figure S29. UV-Vis absorbance of methyl orange (50 μM , red) and supernatant after adsorption by TPECD polymer (1 mg mL⁻¹, black) (1 mg polymer with 1 mL 50 μM dye solution for 5 minutes).

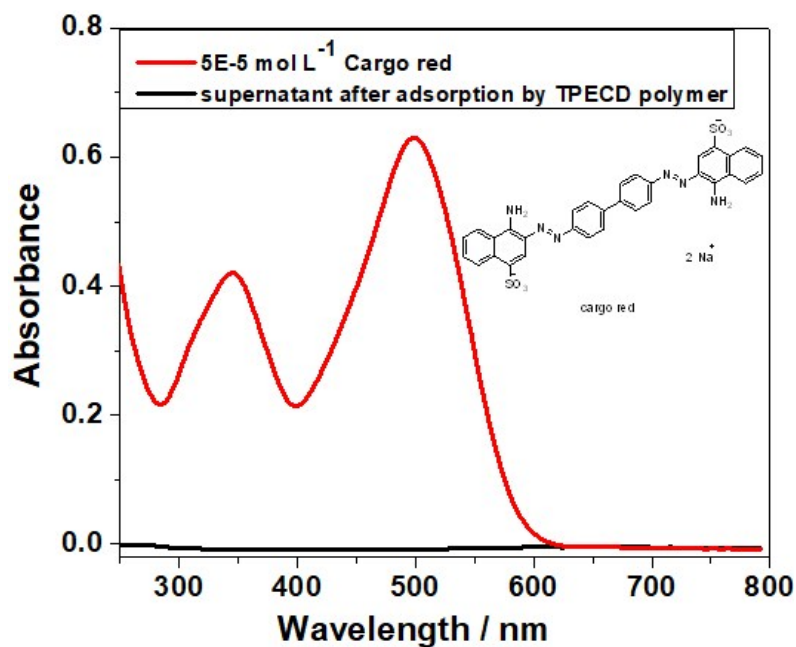


Figure S30. UV-Vis absorbance of cargo red (50 μM , red) and supernatant after adsorption by TPECD polymer (1 mg mL⁻¹, black) (1 mg polymer with 1 mL 50 μM dye solution for 5 minutes).

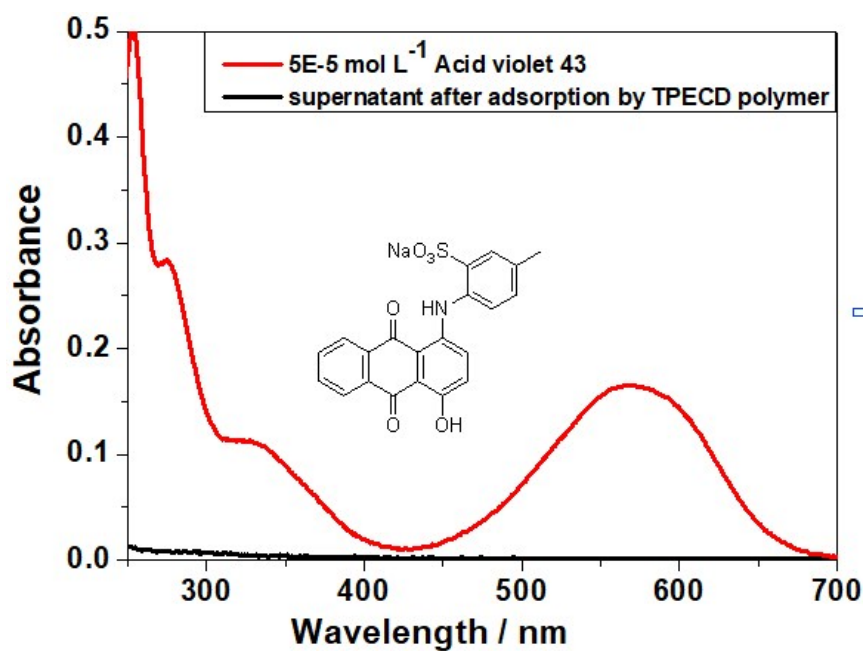


Figure S31. UV-Vis absorbance of acid violet 43 (50 μM , red) and supernatant after adsorption by TPECD polymer (1 mg mL^{-1} , black) (1 mg polymer with 1 mL 50 μM dye solution for 5 minutes).

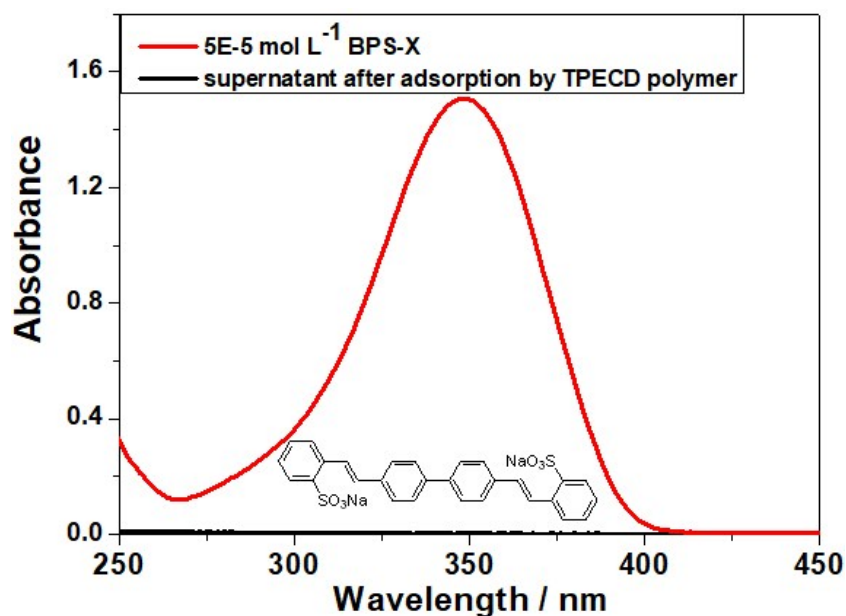


Figure S32. UV-Vis absorbance of BPS-X (50 μM , red) and supernatant after adsorption by TPECD polymer (1 mg mL^{-1} , black) (1 mg polymer with 1 mL 50 μM dye solution for 5 minutes).

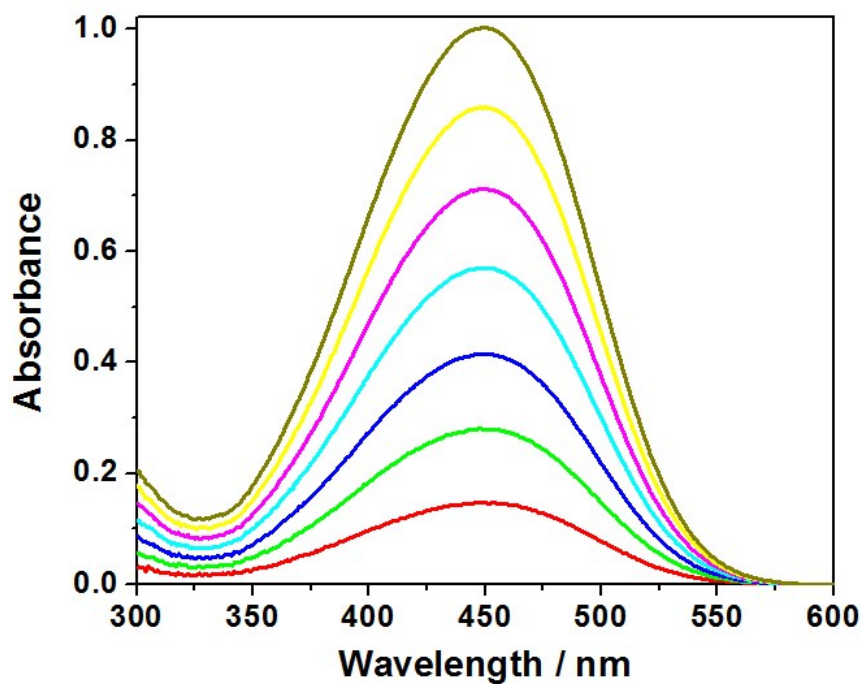


Figure S33. UV-Vis spectra of a series of concentrations (10, 20, 30, 40, 50, 60, 70 μmol/L) of DASPI.

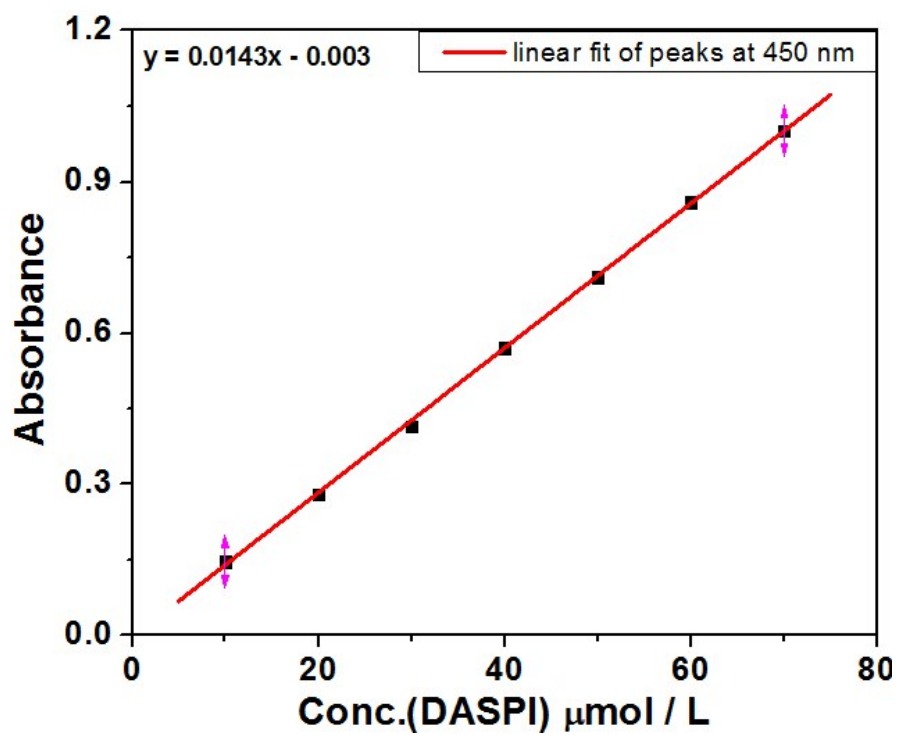


Figure S34. Linear fitting of UV-Vis absorbance of DASPI at 450 nm.

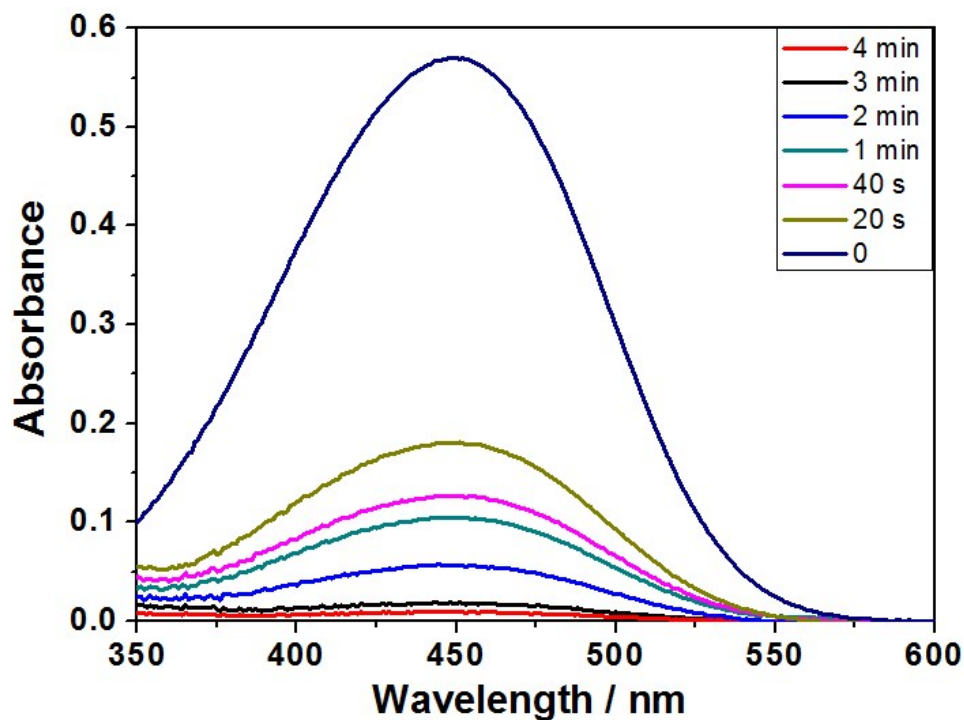


Figure S35. UV-Vis spectra of DASPI (40 μmol/L) after adsorbed by TPESC4A polymer for a certain time (0, 20s, 40s, 1 min, 2 min, 3 min, 4 min).

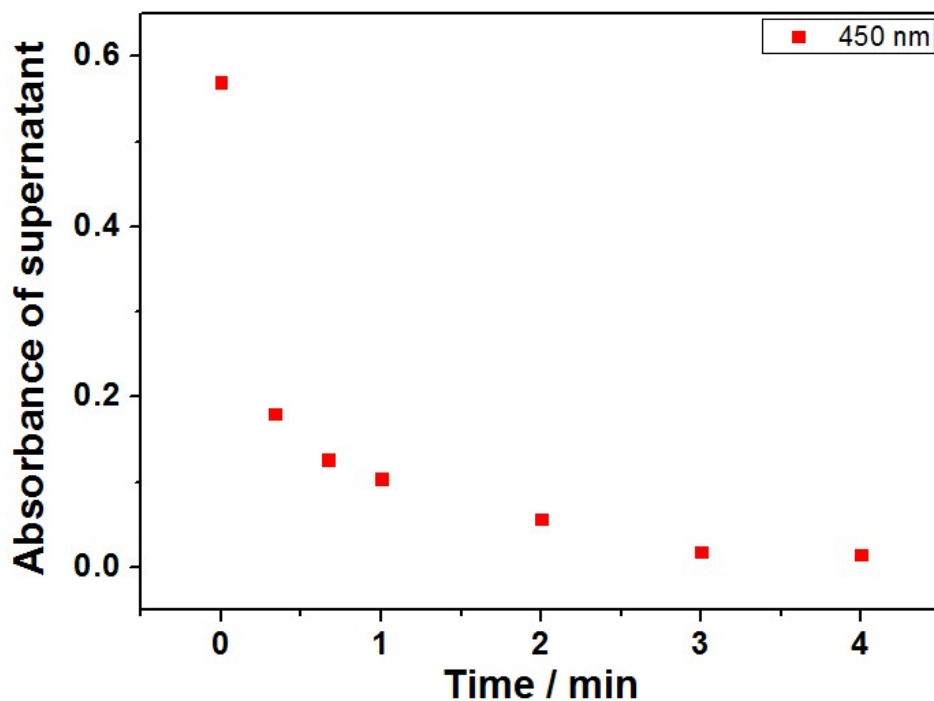


Figure S36. Changes of UV-Vis absorbance of DASPI at 450 nm (50 μmol/L) along with the time (0, 20s, 40s, 1 min, 2 min, 3 min, 4 min).

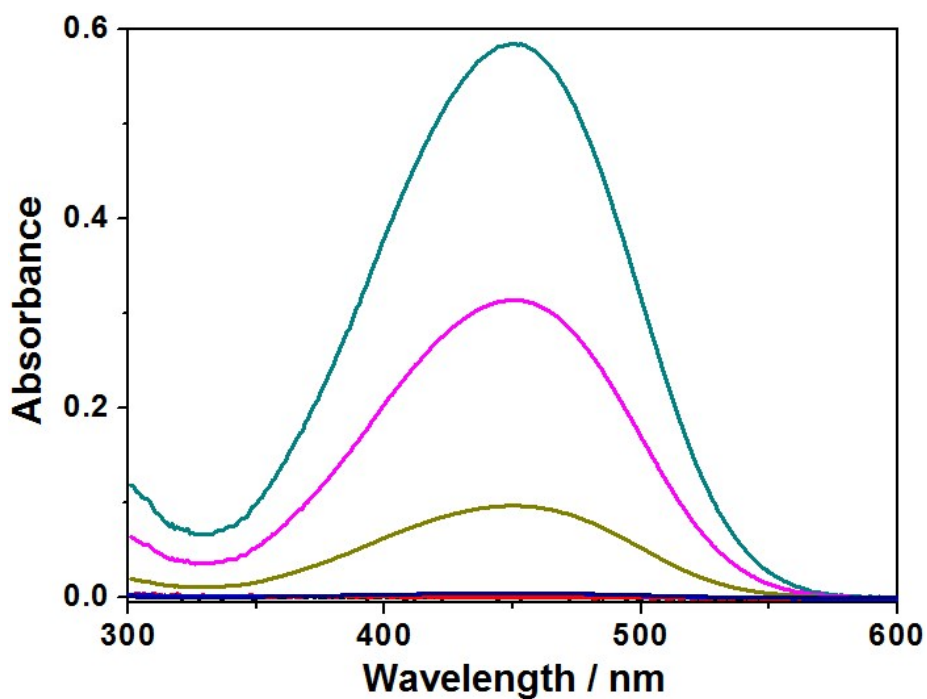


Figure S37. UV-Vis spectra of DASPI supernatant after adsorbed by TPESC4A polymer (1 mg polymer for 1 mL dye solution) (concentrations before absorbed are 5, 10, 20, 40, 60, 80, 100 $\mu\text{mol/L}$ from bottom up).

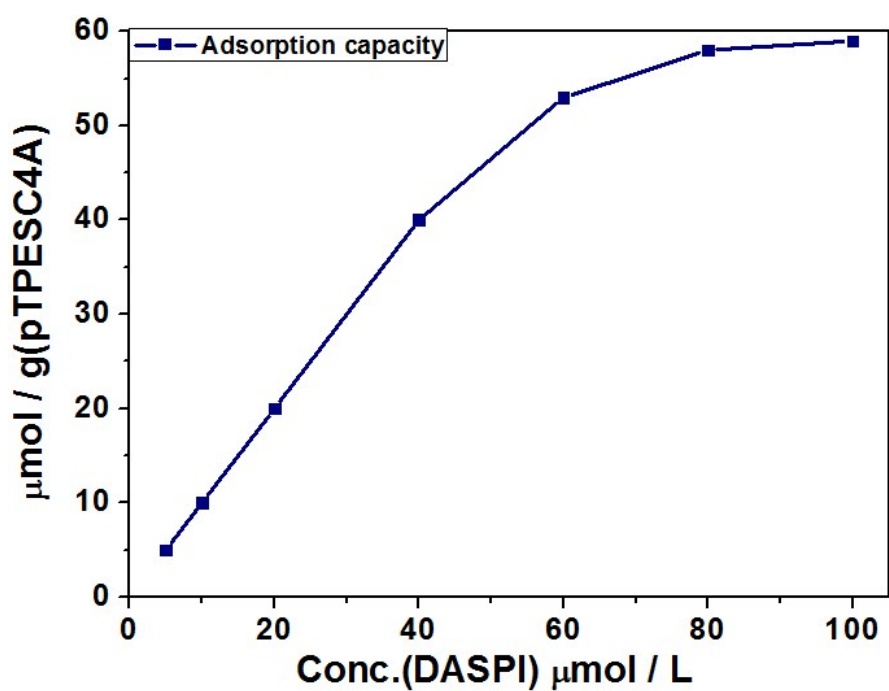


Figure S38. Adsorbed amount of DASPI changed along with the increase concentrations of sRhB calculated from the UV-Vis absorbance work plot.

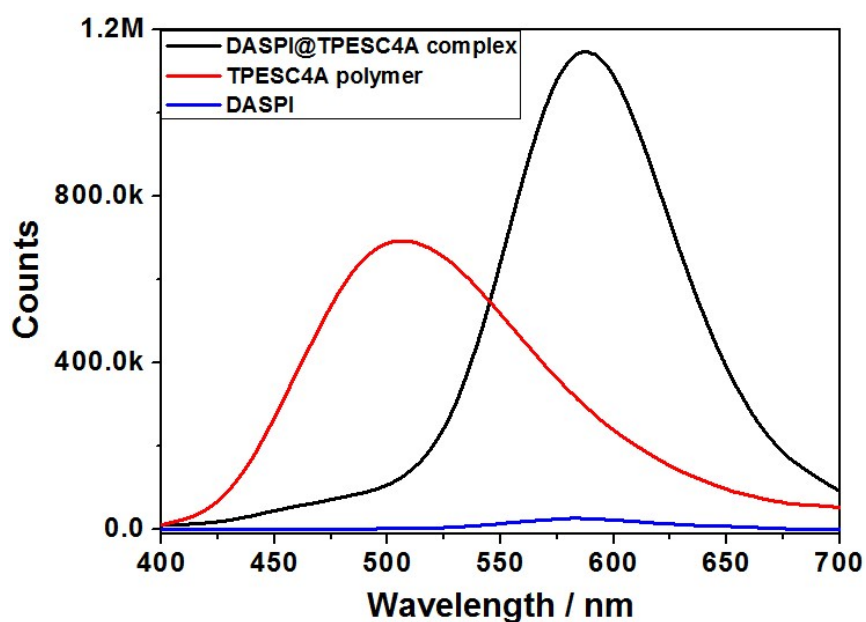


Figure S39. Solid FL emission spectra of TPESC4A polymer (red), DASPI@TPESC4A complex (black) and DASPI mixed with polyvinyl alcohol (PVA) for dispersion (blue).

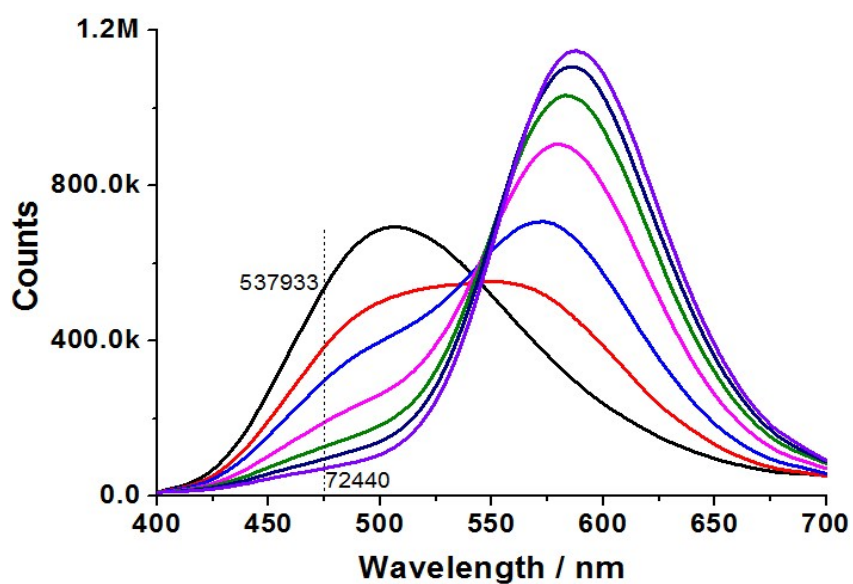


Figure S40. FL emission spectra of DASPI@pTPESC4A (0、4、8、16、24、32 and 40 $\mu\text{mol g}^{-1}$ top-down), quantum yield of DASPI@pTPESC4A (40 $\mu\text{mol g}^{-1}$)

$$\varphi = (1 - 72440/537933) * 100 \% = 87 \%$$

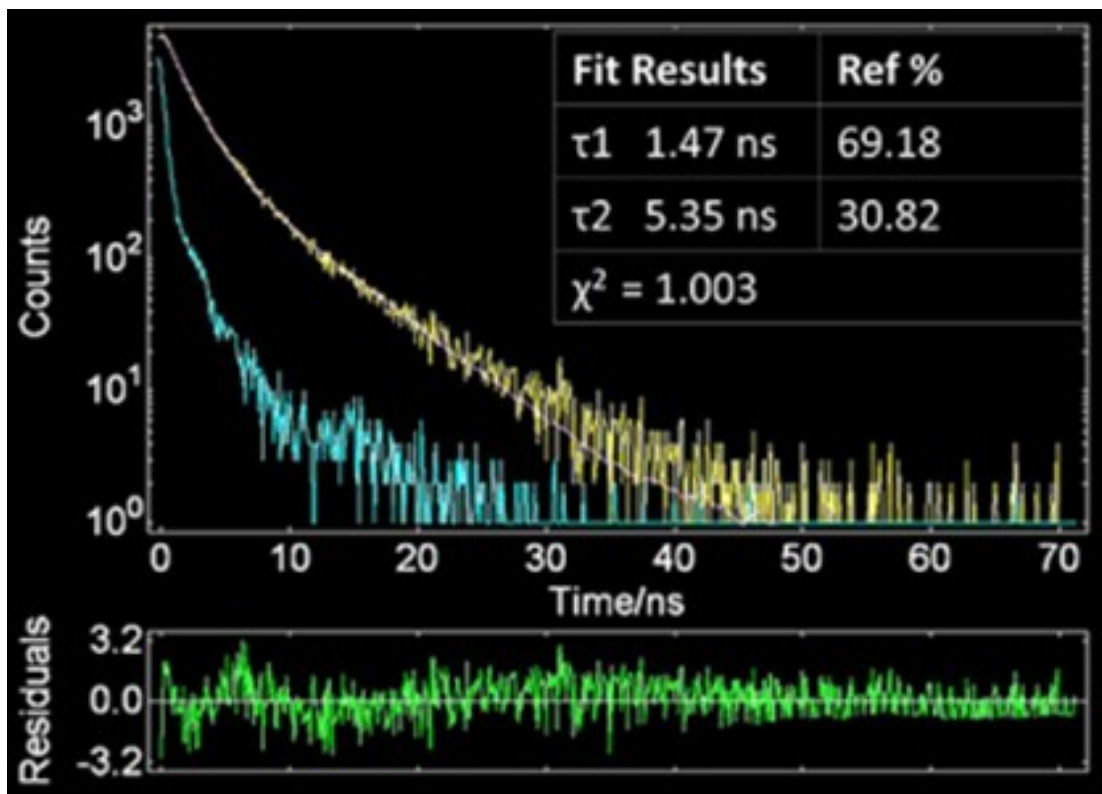


Figure 41. Fluorescence decay trace of TPESC4A polymer (ex. at 360 nm, decay wavelength = 500 nm). The fluorescence decay of TPESC4A was fitted by two exponential components, that were τ_1 2.26 ns and τ_2 7.78 ns with 47% and 53% of the total intensity decay, respectively. Such bi-exponential decay was attributed to the inhomogeneous surrounding environment of TPE group¹. As it is complex to pick out meaningful rate constants in such heterogeneous solid, the average lifetime calculated 5.17 ns can be considered to make meaningful sense out of the data.

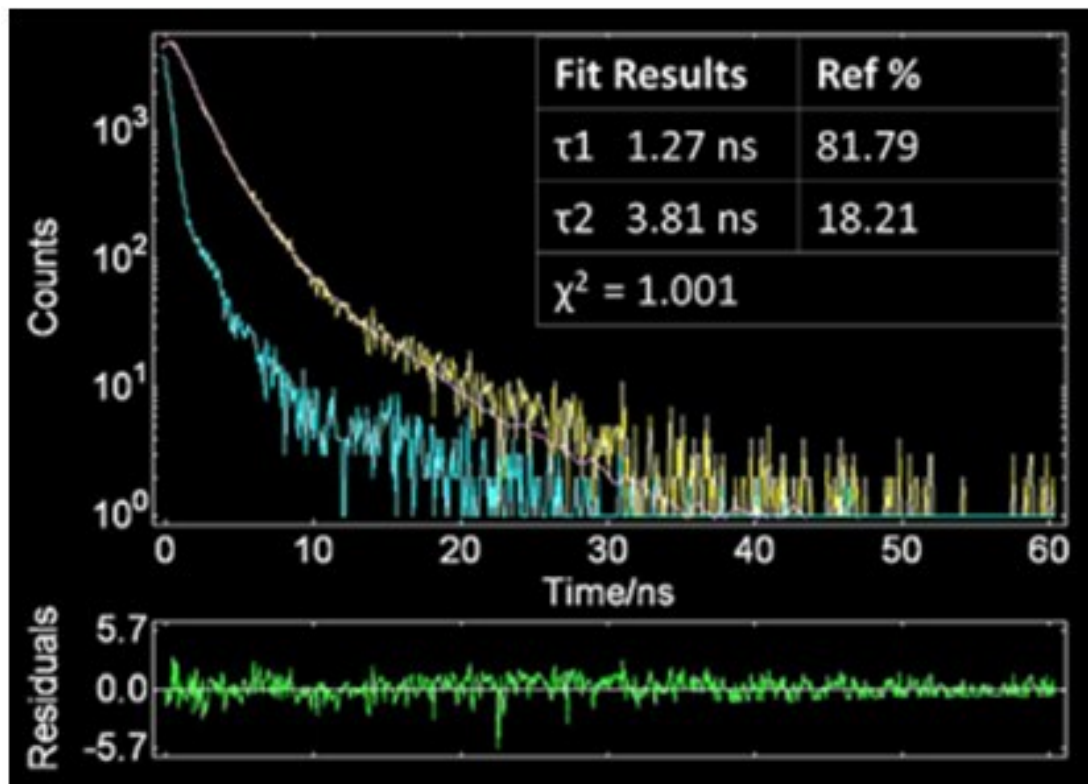


Figure 42. Fluorescence decay trace of DASPI@TPESC4A complex (40 $\mu\text{mol g}^{-1}$, ex. at 360 nm, decay wavelength = 580 nm). The fluorescence decays at different wavelength of DASPI@TPESC4A (40 $\mu\text{mol g}^{-1}$) were also best fitted with bi-exponential terms, owing to the two excited states of DASPI, the local excited (LE) state and TICT state (Figure S29-S32 & Table S1).²

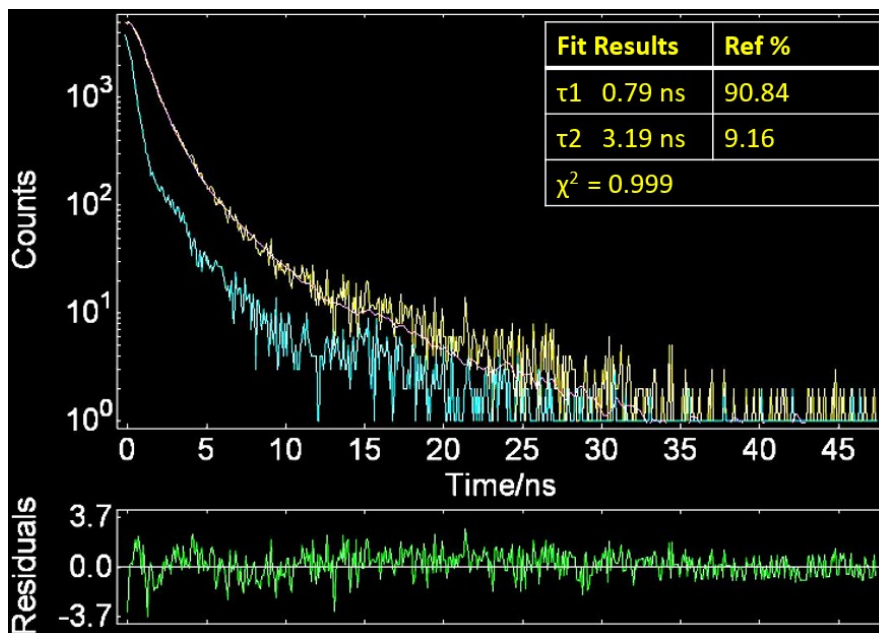


Figure S43. Fluorescence decay profile of DASPI@TPESC4A complex (40 $\mu\text{mol g}^{-1}$, ex: 360 nm, decay wavelength: 520 nm).

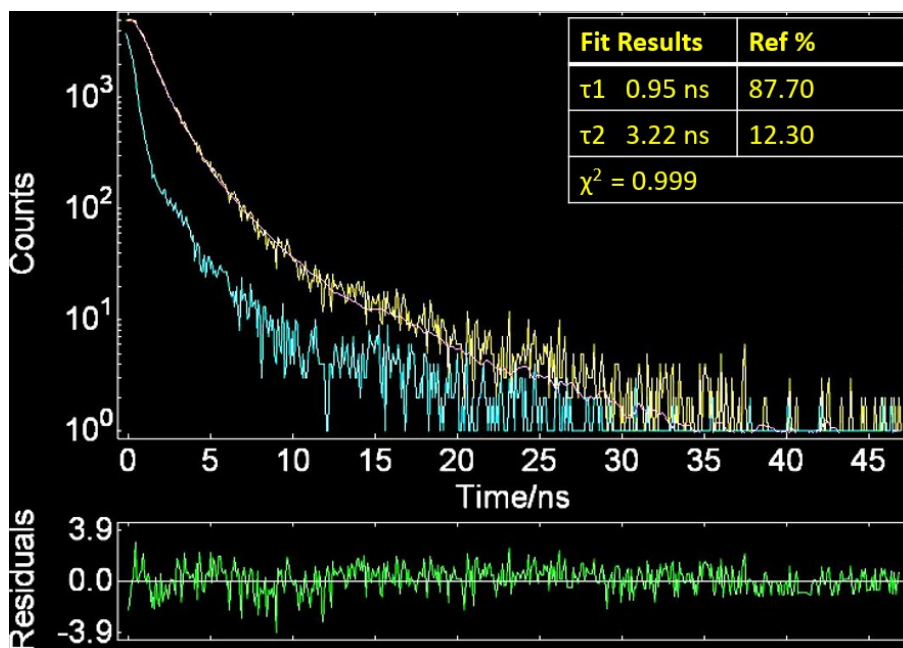


Figure S44. Fluorescence decay profile of DASPI@TPESC4A complex (40 $\mu\text{mol g}^{-1}$, ex: 360 nm, decay wavelength: 540 nm).

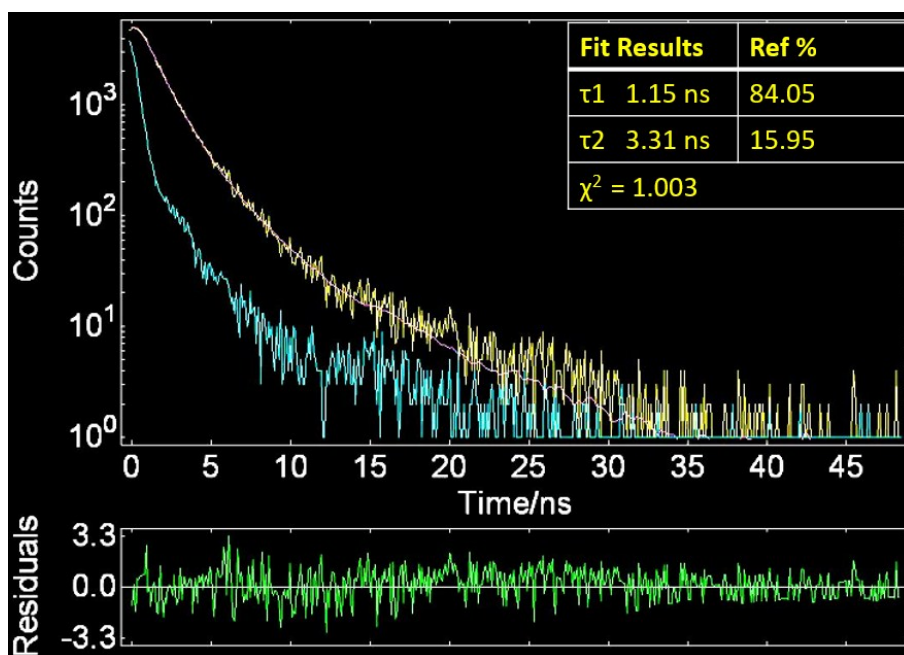


Figure S45. Fluorescence decay profile of DASPI@TPESC4A complex (40 $\mu\text{mol g}^{-1}$, ex: 360 nm, decay wavelength: 560 nm).

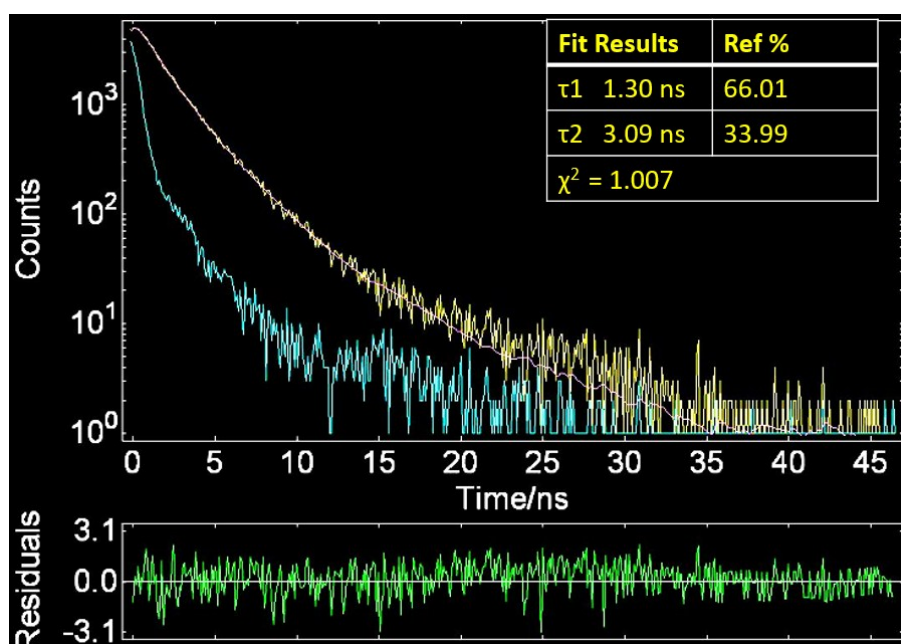


Figure S46. Fluorescence decay profile of DASPI@TPESC4A complex (40 $\mu\text{mol g}^{-1}$, ex: 360 nm, decay wavelength: 600 nm).

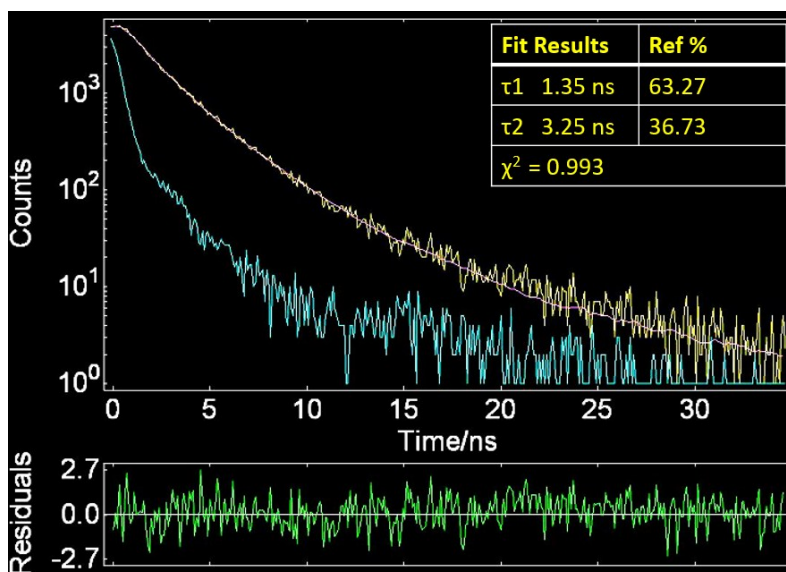


Figure S47. Fluorescence decay profile of DASPI@TPESC4A complex (40 $\mu\text{mol g}^{-1}$, ex: 360 nm, decay wavelength: 620 nm).

Table S1. List of lifetimes of DASPI@TPESC4A complex (40 $\mu\text{mol g}^{-1}$) at different wavelengths (520, 540, 560, 580, 600 and 620 nm).

Wavelength/(nm)	520	540	560	580	600	620
τ_1 /(ns)	0.79	0.95	1.15	1.27	1.30	1.35
W_1 (%)	90.84	87.70	84.05	81.79	66.01	63.27
τ_2 /(ns)	3.19	3.22	3.31	3.81	3.09	3.25
W_2 (%)	9.16	12.30	15.95	18.21	33.99	36.73
χ^2	0.999	0.999	1.003	1.001	1.007	0.993

As shown in Table S1, the ratio of the shorter lifetime, which is recognized as emission arose from LE state of DASPI based on the energy level diagram, is decreasing along with the increase of wavelength from 520 nm to 620 nm, and vice versa for the TICT state. Compared to the solution state or aggregated state of DASPI alone, this confined system lighted up DASPI by avoiding fast state change or aggregation caused quenching.

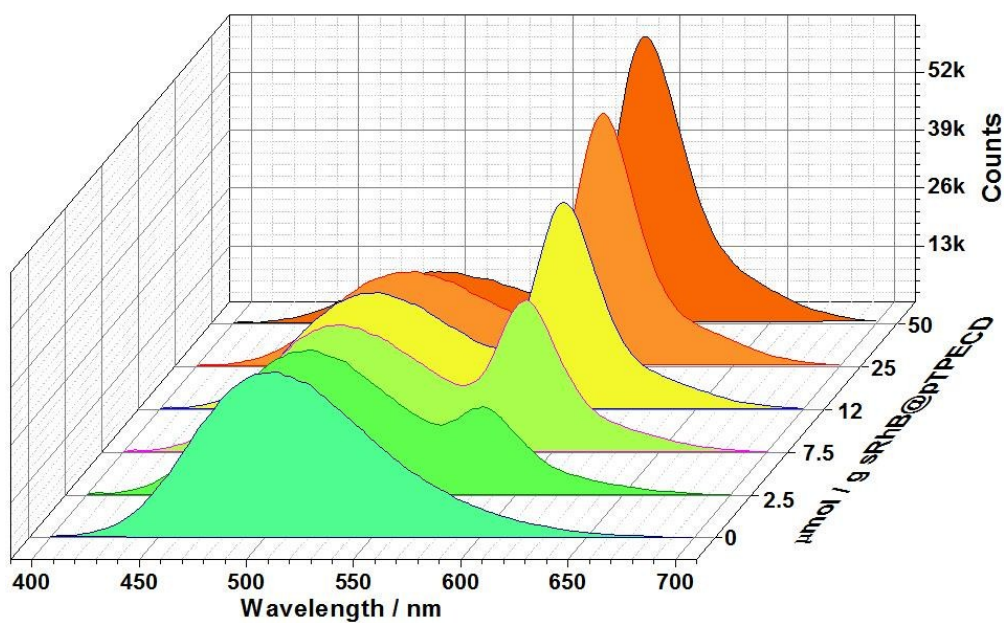


Figure S48. FL emission spectra of sRhB@pTPECD complex (0, 2.5, 7.5, 12, 25 and 50 $\mu\text{mol g}^{-1}$ from front to back).

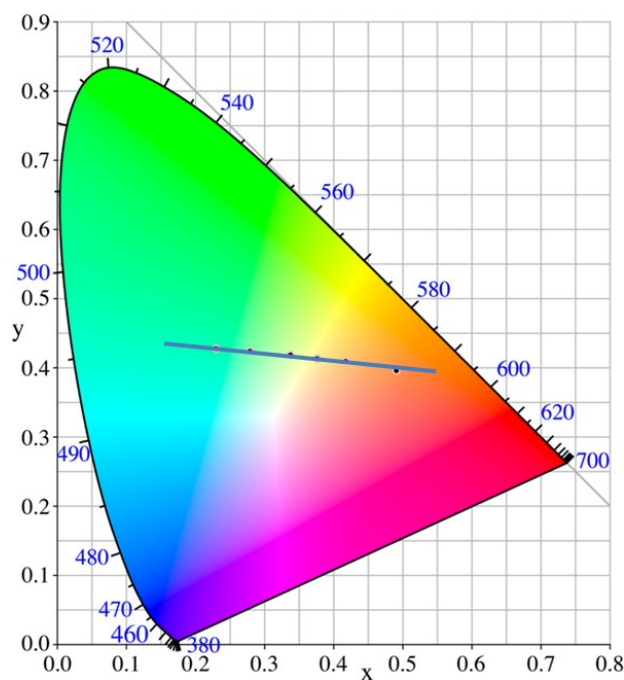


Figure S49. CIE diagram showing the trajectories of the color changes based on the FL emission spectra of sRhB@pTPECD complex (0, 2.5, 7.5, 12, 25 and 50 $\mu\text{mol g}^{-1}$).

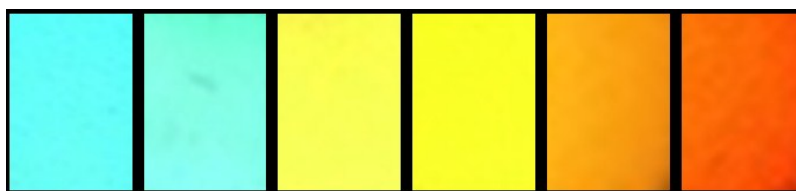


Figure S50. Photos of sRhB@TPECD complex (0, 2.5, 7.5, 12, 25 and 50 $\mu\text{mol g}^{-1}$ from left to right).

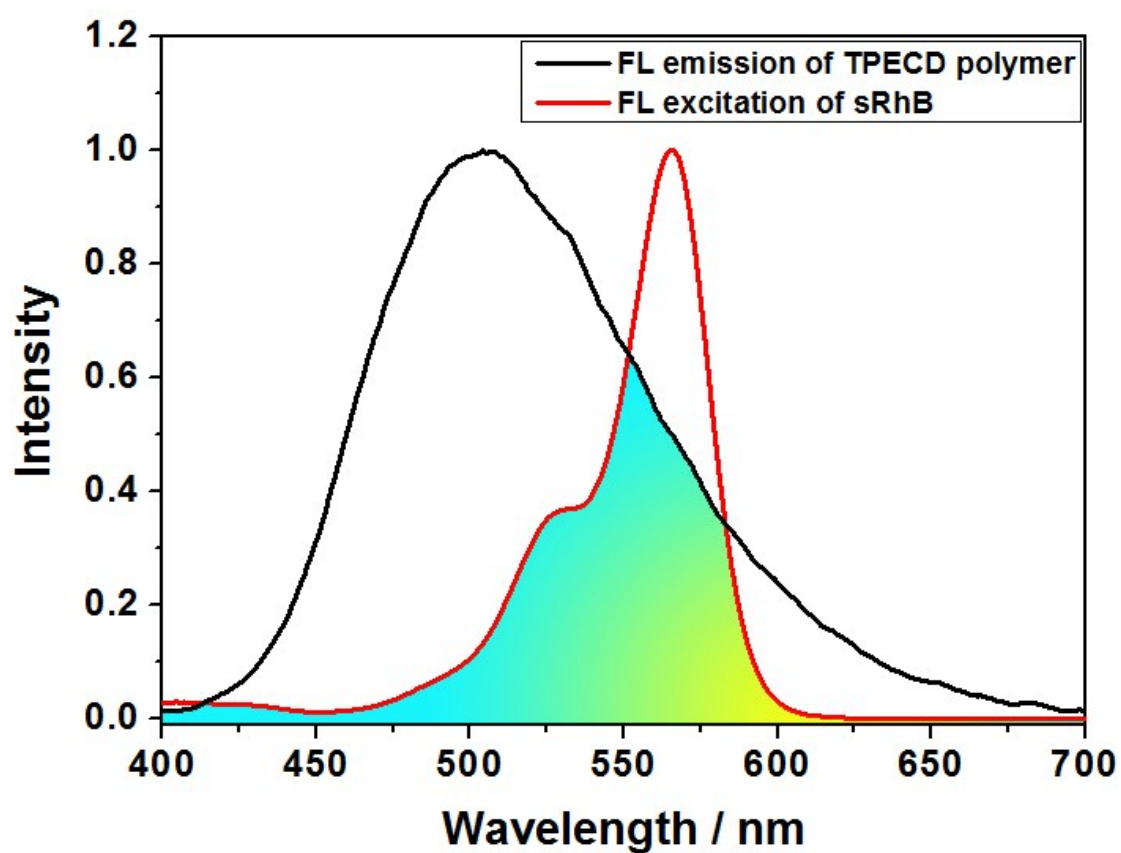


Figure S51. Overlap of the excitation spectrum of sRhB mixed with polyvinyl alcohol (PVA) for dispersion and the FL band of TPECD polymer.

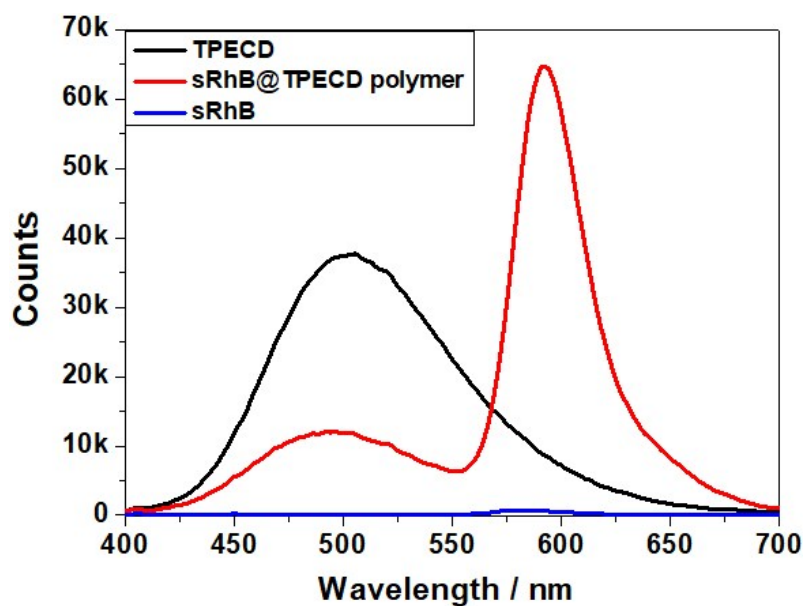


Figure S52. Solid FL emission spectra of TPECD polymer (black), sRhB@TPECD ($50 \mu\text{mol g}^{-1}$) complex (red) and sRhB mixed with polyvinyl alcohol (PVA) for dispersion (blue).

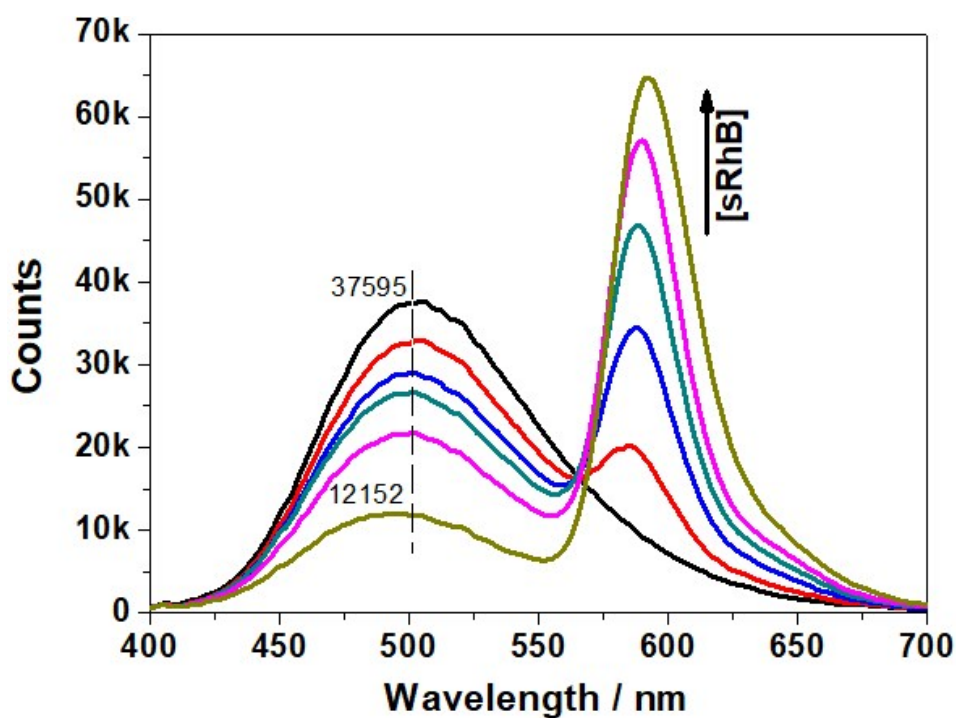


Figure S53. FL emission spectra of sRhB@TPECD complex (0, 2.5, 7.5, 12, 25 and $50 \mu\text{mol g}^{-1}$ top-down, quantum yield of sRhB@TPECD complex ($50 \mu\text{mol g}^{-1}$) $\phi = (1 - 12152/37595) \cdot 100 \% = 68 \%$).

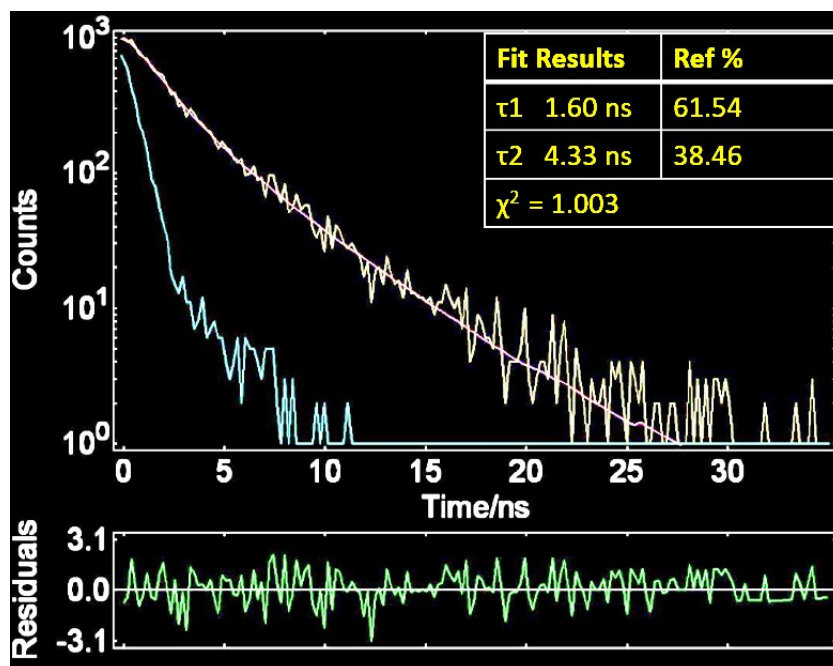


Figure S54. Fluorescence decay profile of TPECD polymer (ex: 360 nm, decay wavelength: 500 nm). The fluorescence decay of TPECD at 500 nm was fitted by two exponential terms. Two lifetimes were τ_1 1.60 ns and τ_2 4.33 ns with the first component occupied around 61.5 % of the total intensity decay. The average lifetime calculated for TPECD is 2.65 ns.

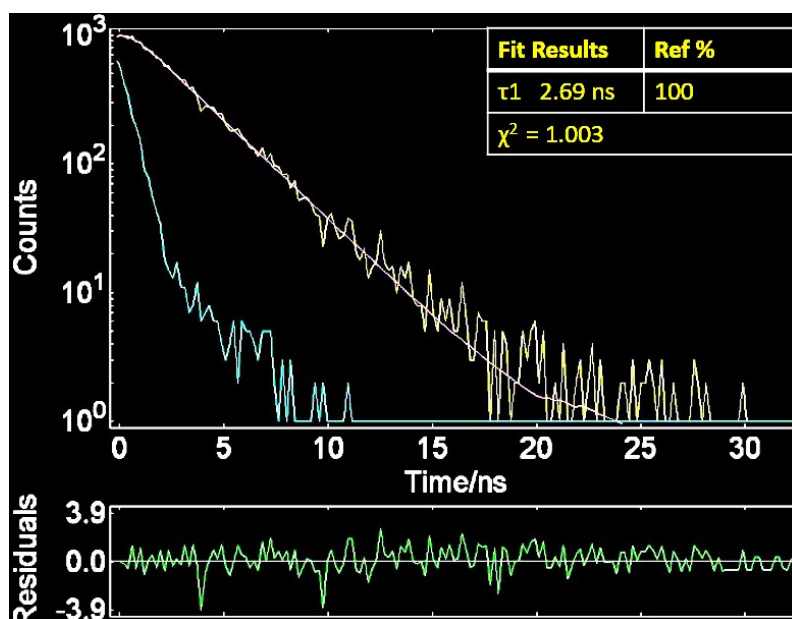


Figure S55. Fluorescence decay profile of sRhB@TPECD complex ($50 \mu\text{mol g}^{-1}$, ex: 360 nm, decay wavelength: 600 nm). For sRhB@TPECD ($50 \mu\text{mol g}^{-1}$), one lifetime 2.69 ns was fitted.

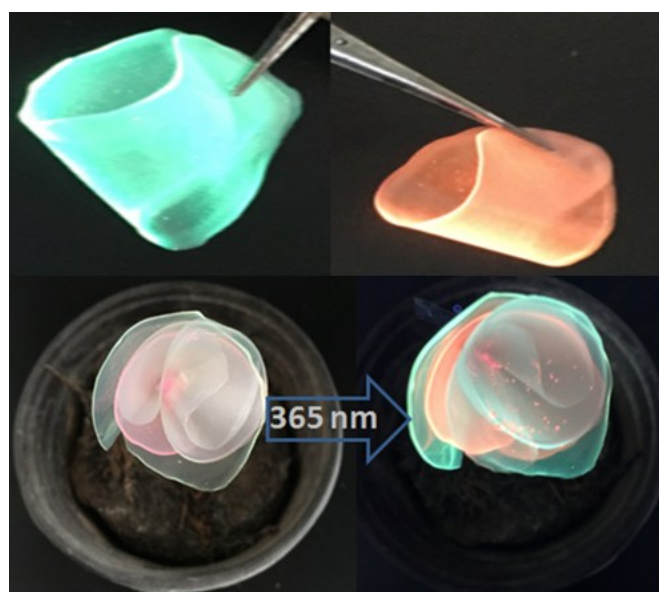


Figure S56. Photos of TPECD polymer (blue) and sRhB@pTPECD complex (orange) taken under 365 nm light; photos of a fluorescent flower made by films and decorated by sRhB@pTPECD complex powder taken under natural light and 365 nm light.

[1] P. Zhang, K. Wu, J. Guo and C. Wang. *ACS Macro Lett.*, **2014**, 3, 1139-1144.

[2] H. Dong, Y. Wei, W. Zhang, C. Wei, C. Zhang, J. Yao and Y. S. Zhao. *J. Am. Chem. Soc.*, **2016**, 138, 1118-1121.