Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Macrocycles Crosslinked Mesoporous Polymers for Ultrafast Separation of Organic Dyes

Qian Zhao[1], Yu Liu[1,2]*

[1] Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, P. R. China

[2] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071, P. R. China

*Address correspondence to yuliu@nankai.edu.cn

Contents

1. General Infromation.

^{1}H NMR spectra were recorded on a Bruker AVANCE AV400 (400 MHz). Signal positions were reported in part per million (ppm) relative to the residual solvent peaks used as an internal standard with the abbreviations s, d, t, quart and quint, denoting singlet, doublet, triplet, quartlet and quintlet, respectively. The residual ^{1}H peak of deuterated solvent appeared at 4.79 ppm in D_2O. All coupling constants *J* are quoted in Hz. Scanning electron microscopy (SEM) images were obtained using a JSM-7500F or MERLIN Compact scanning electron microscope. Surface area measurements were conducted on a Quantachrome instruments. Each sample (50 mg) was degassed at 100 °C for 24 h and then backfilled with N_2. Surface parameters were determined using Multi-point BET and pore size distribution was determined using NLDFT method. Thermo gravimetric analysis was measured on a NETZSCH TG 209 instrument. UV/Vis spectra were recorded in a quartz cell (light path 1cm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller.

2. Fabrication of cyclophane thin-films.

Synthesis of pTC-C4A / pTC-SC4A / pTC-P5A films: C4A, SC4A and P5A were synthesized according to the literatures[1]. The purity of SC4A was determined as 87 % by NMR spectroscopy using sodium 3-(trimethylsilyl)-1-propanesulfonate as standard. SC4A Films were fabricated via PES or Nylon 6 membranes (with the pore size was 200 nm) supported interfacial polymer condensation. First, commercial porous PES/Nylon 6 membranes were immersed in cyclophanes and NaOH aqueous solution for 30 min and pick up from the solution for next use. Then, the membranes were immersed in a 0.5% (w/v) TC at room temperature for a certain time as listed in Table S1. Finally, the membranes were washed with hexane, EtOH and water several times to remove the unreacted substrate and stored in EtOH for further use. Control experiments were done without cyclophane in aqueous solution or without TC in organic phase and no film formed. To characterize properties of the films alone, enough films were isolated by dissolving the PES support membranes with DMF. Then the isolated films were washed with EtOH and water several times. Finally, isolated films were transferred to water and frozen dried for further measurement.

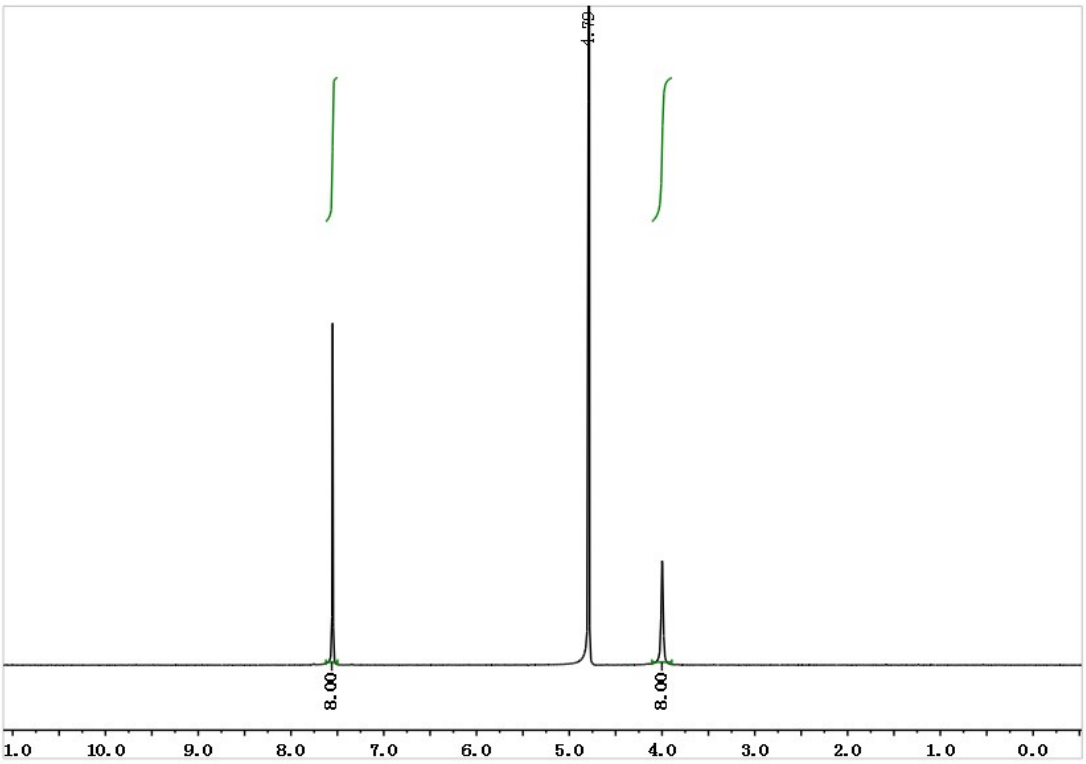

Figure S1. ^{1}H NMR of SC4A.

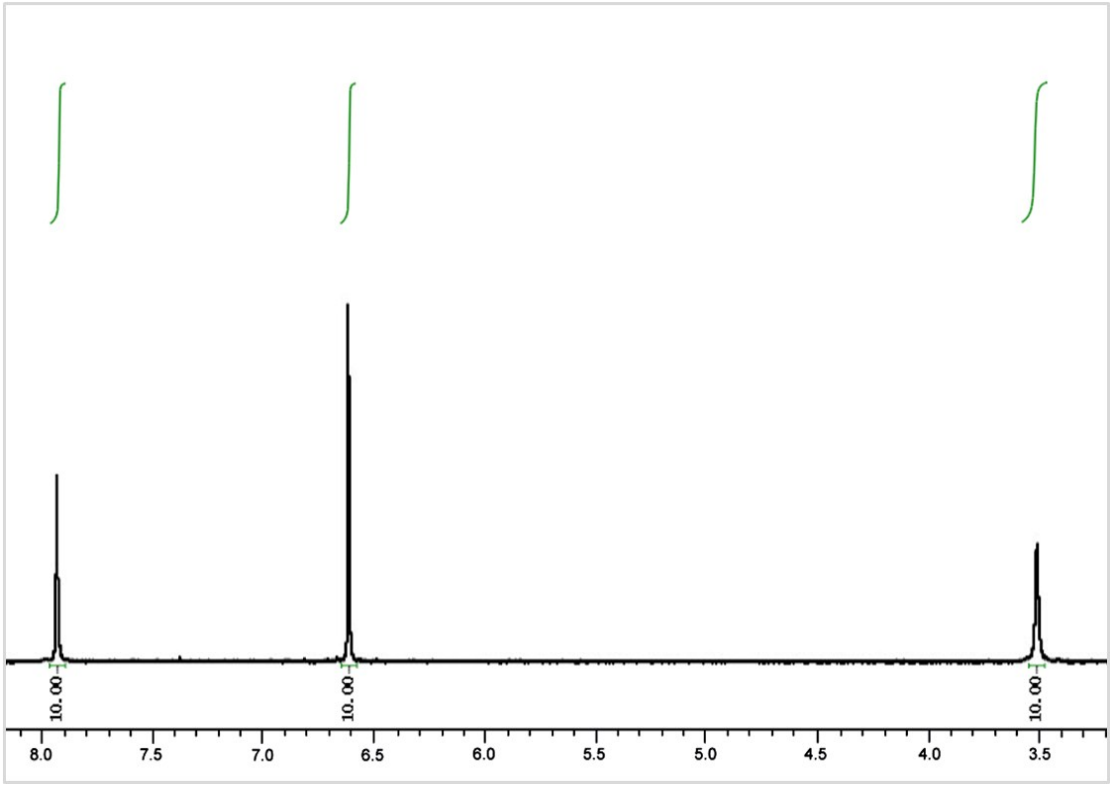

Figure S2. ^{1}H NMR of P5A.

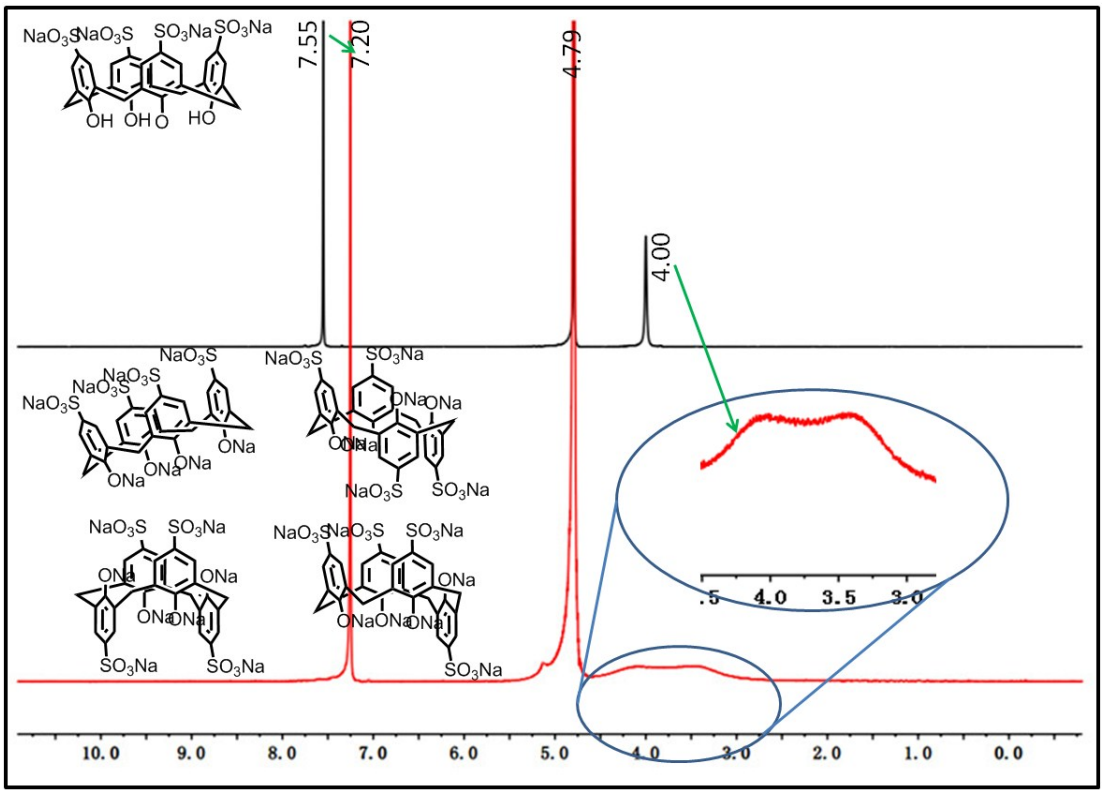

Figure S3. ^{1}H NMR spectra of SC4A (black, 1.0 x 10^{-2}mol L^{-1}) and SC4A-NaOH (red, 1 x 10^{-2}mol L^{-1} for SC4A and 4.8 x 10^{-2}mol L^{-1} for NaOH). The proton peaks associated with methylene bridge of SC4A at around 4 ppm broadened to 3-5 ppm along with split upon the addition of NaOH. And also proton peaks associated with phenol ring at 7.55 ppm shifted to 7.20 ppm. According to the literature[2], four discrete forms of SC4A can exist, which have been designated as "cone", "partial-cone", "1, 2-alternate" and "1, 3-alternate" conformations and the structures of these four conformations are inserted in the blank space of the NMR spectra. As our pTC-SC4A film was formed in alkaline condition, we speculated that the film was a random polycondensation with four different patterns of SC4A due to the broken of both intermolecular and intramolecular hydrogen binding between SC4A monomers.

3. Optimizing fabrication conditions of the films.

Table S1. Screening conditions for fabrication of pTC-SC4A films: (a) conditions for fixed SC4A's concentration and varied NaOH's in aqueous solutions; (b) conditions for fixed mass ratio of SC4A: NaOH = 5:1[a] and varied the concentrations in aqueous solution; (c) screening of organic solvents which can dissolve TC including hexane, acetone, toluene. All interfacial polymerization were done at room temperature with a PES support and with TC concentration fixed at 0.5 % because TC was the far excessive substrate and its concentration didn't influence that much of the interfacial polymerization. The optimal conditions were marked red in the table.

		Terephtaloyl chloride (w/v = 0.5 %)
a) **SC4A (50 mg ml^{-1})[b] with NaOH (mg ml^{-1}) as right column in aqueous solutions.**	2	Film with tiny holes
	5	Film with tiny holes
	10	Thin film with no defect
	20	Film with dots
	40	Film with dots
b) **Fixed the ratio of W_{SC4A} :W_{NaOH} in 5:1, and varied the concentrations based on SC4A (mg ml^{-1}) as right column in aqueous solutions.**	10	No film formed
	25	No film formed
	50	Transparent film with no defect (thickness = 512 nm)
	75	Semi-transparent film
	100	Semi-transparent but fragile film
c) **Solvent**	n-hexane	Thin film formed in 20 minutes
	acetone	Fragile film formed within 10 seconds along with the dissolving of the PES support
	toluene	Thin film formed in 20 minutes

a. Those mass ratios equate to the mole ratio for 1: 4.8 which is 1:1.2 for NaOH to hydroxyl group in SC4A**.**

b. This mass concentration equates to 5.2 x 10^{-5} mol L^{-1} in mole concentration.

Table S2. Screening conditions for fabrication of pTC-P5A films: (a) conditions for fixed P5A's concentration and varied NaOH's in aqueous solutions; (b) conditions for fixed mass ratio of P5A: NaOH = 5:4[a] and varied the concentrations in aqueous solution; (c) screening of organic solvents which can dissolve TC including hexane, acetone, toluene. All interfacial polymerization were done at room temperature with a PES support and with TC concentration fixed at 0.5 % because TC was the far excessive substrate and its concentration didn't influence that much of the interfacial polymerization. The optimal conditions were marked red in the table.

		Terephtaloyl chloride (w/v = 0.5 %)
a) **P5A (20 mg ml^{-1})[b] with NaOH (mg ml^{-1}) as right column in aqueous solutions.**	4	Film with tiny holes
	8	Film with tiny holes
	16	Thin film with no defect
	32	Film with dots
	48	Film with dots
b) **Fixed the ratio of W_{P5A} :W_{NaOH} in 5:4, and varied the concentrations based on P5A (mg ml^{-1}) as right column in aqueous solutions.**	4	Film with tiny holes
	8	Film with tiny holes
	16	Thin film with no defect
	32	Film with dots
	48	Film with dots
c) **Solvent**	n-hexane	Thin film formed in 20 minutes
	acetone	Fragile film formed within 10 seconds along with the dissolving of the PES support
	toluene	Thin film formed in 20 minutes

a. Those mass ratios equate to the mole ratio for 1: 12 which is 1:1.2 for NaOH to hydroxyl group in P5A**.**

b. This mass concentration equates to 3.3 x 10^{-5} mol L^{-1} in mole concentration.

Both SC4A and P5A can dissolve well in NaOH aqueous solution, but no matter under what conditions like screened above, C4A can only reach a dissolve balance in

alkaline solution. So supernatant of C4A alkaline solution was used to do further experiments.

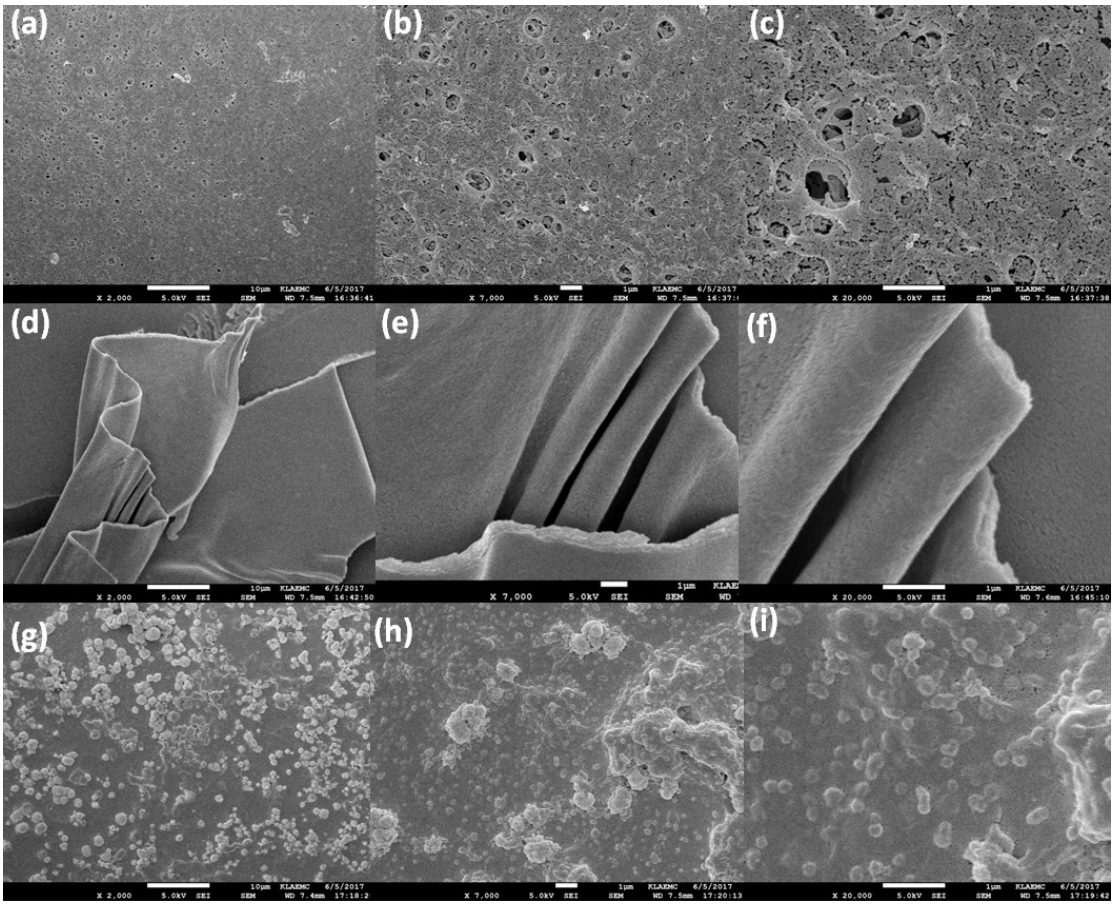

Figure S4. SEM images of pTC-SC4A films prepared by PES supported interfacial polymerization (5% SC4A in NaOH aqueous solution and 0.5% TC in n-hexane at room temperature) at different scales from left to right: (a-c) 0.5% NaOH; (d-f) 1% NaOH; (g-i) 2% NaOH. SEM samples were prepared by pipette a small piece of films stored in EtOH solution with plastic dropper and dropped on wafer.

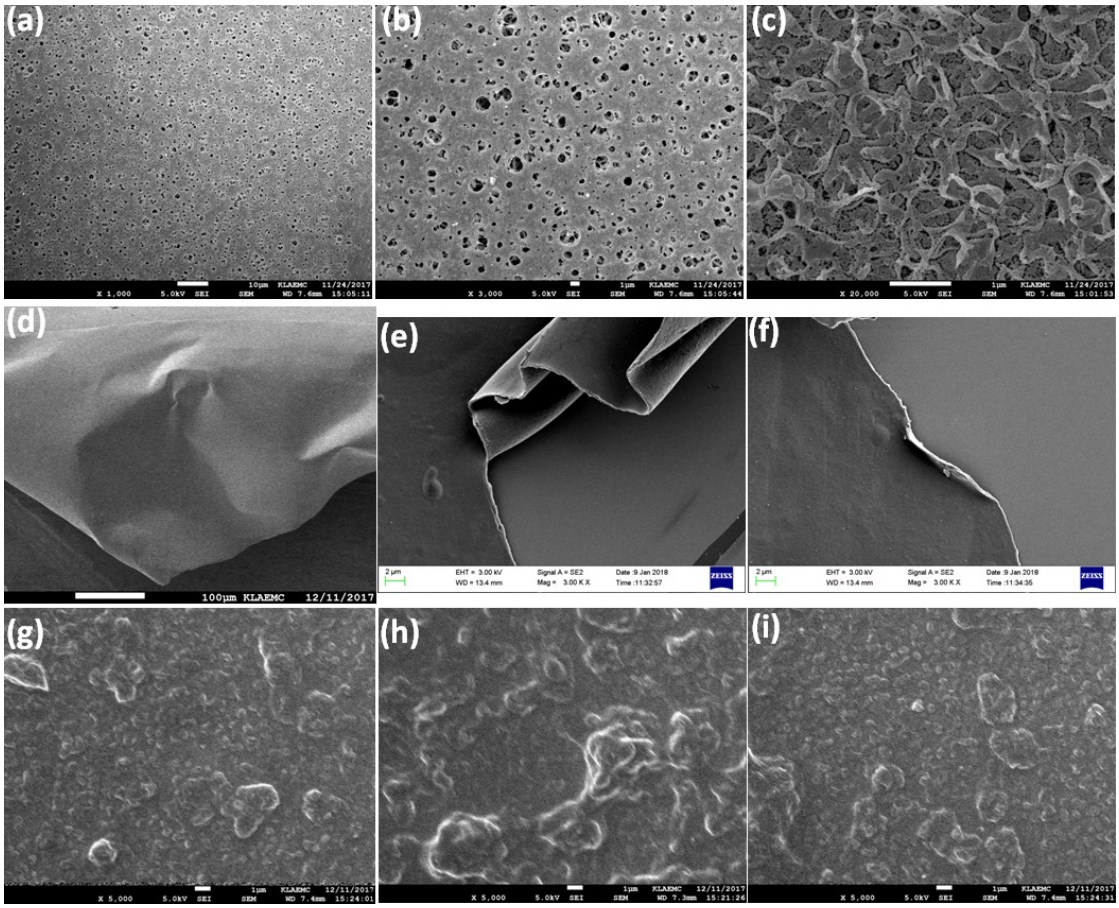

Figure S5. SEM images of pTC-P5A films prepared by PES supported interfacial polymerization (2% P5A in NaOH aqueous solution and 0.5% TC in n-hexane at room temperature) at different scales: (a-c) 0.8 % NaOH; (d-f) 1.6 % NaOH; (g-i) 3.2 % NaOH. SEM samples were prepared by pipette a small piece of films stored in EtOH solution with plastic dropper and dropped on wafer.

Table S3. Raw data and calculations of solvent permeations according to the formula υ = V / (T * S*ΔP). υ standing for permeance, V standing for the volume of the solvents, S referring to the effective filtration area, and ΔP standing for the pressure gap assigned as 1bar which is the maximum pressure gap under vacuum filtration.

		T	S	V	Permeance (υ)	
		min	cm2	mL	mL•cm^{-2} min^{-1}bar^{-1}	L•m^{-2} h^{-1}bar^{-1}
pTC-SC4A	H_2O	8	1.77	36	2.54	1525
	EtOH	6	1.77	36	3.39	2034
	DMF	3.83	1.77	36	5.31	3186
	MeOH	2.5	1.77	36	8.14	4881
	acetone	1.5	1.77	36	13.56	8136
	CH_2Cl_2	1.83	1.77	36	11.11	6669
	CH_3CN	1.25	1.77	36	16.27	9763
pTC-P5A	H_2O	20	1.77	36	1.02	610
	EtOH	17	1.77	36	1.20	718
	DMF	9	1.77	36	2.26	1356
	MeOH	8	1.77	36	2.54	1525
	acetone	4	1.77	36	5.08	3051
	CH_2Cl_2	5.33	1.77	36	3.82	2290
	CH_3CN	4	1.77	36	5.08	3051

4. Characterization of films.

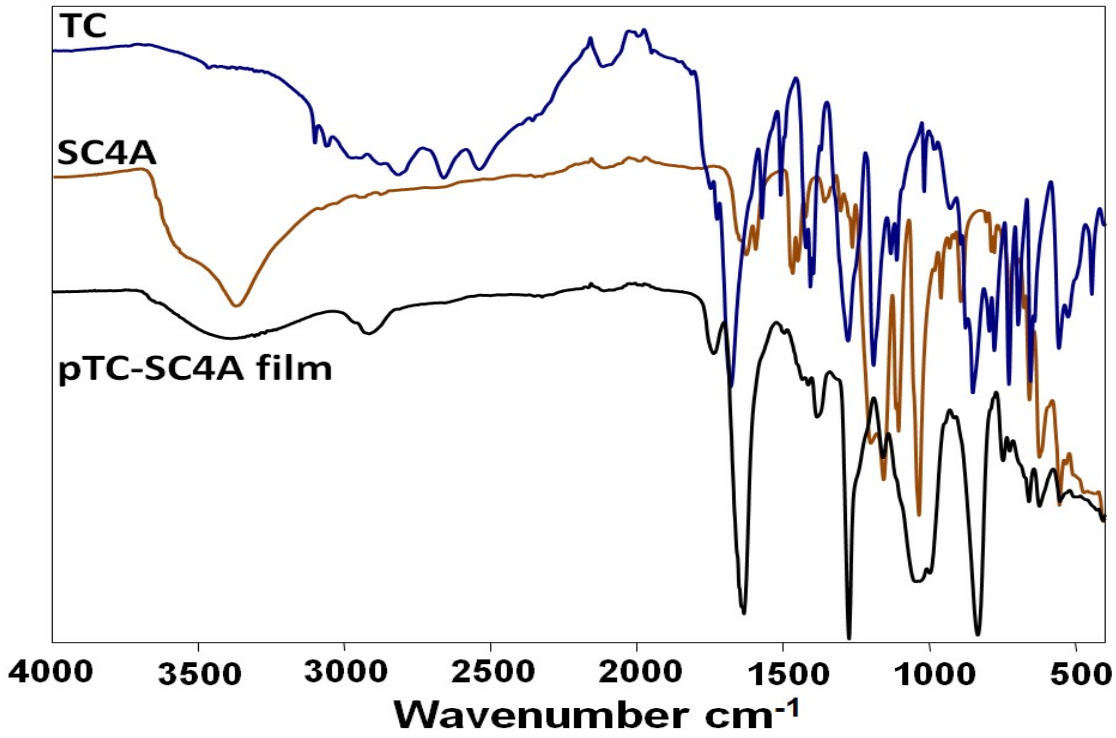

Figure S6. FT-IR spectra of TC, SC4A and pTC-SC4A film.

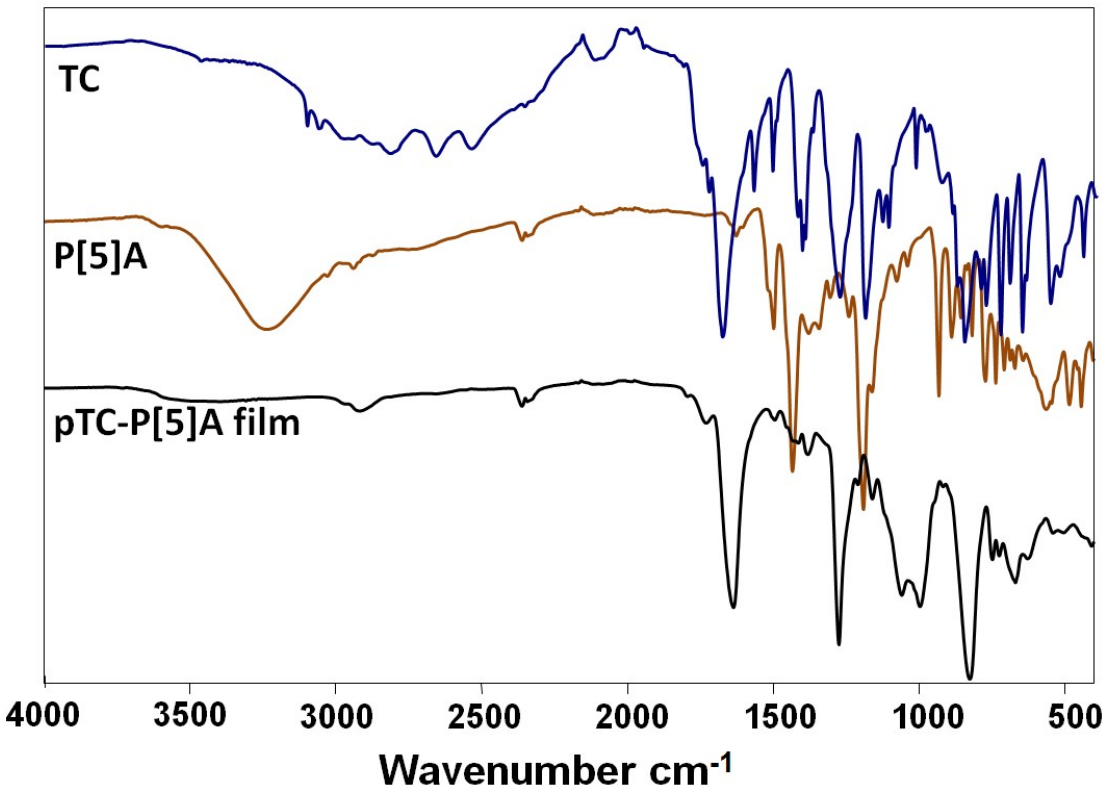

Figure S7. FT-IR spectra of TC, P5A and pTC-P5A film.

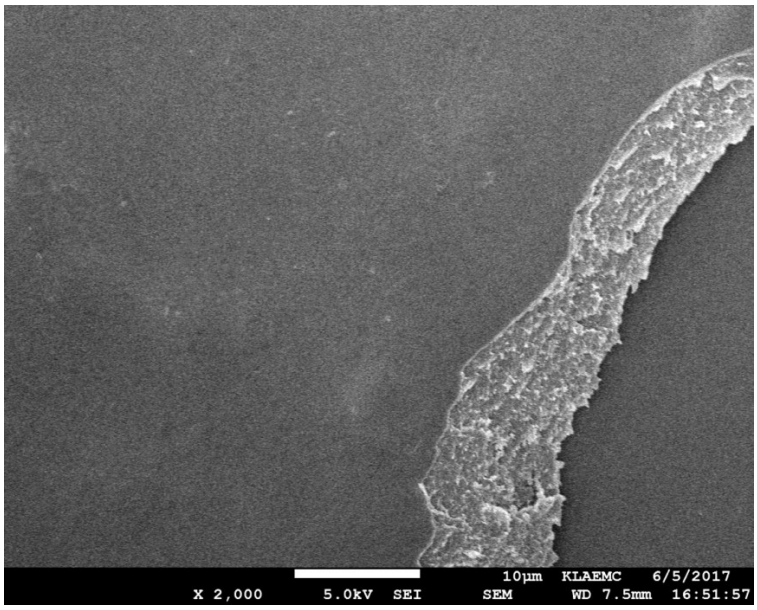

Figure S8. SEM images of the expanded edge of pTC-SC4A film. SEM samples were prepared by pipette a small piece of films stored in EtOH solution with plastic dropper and dropped on wafer.

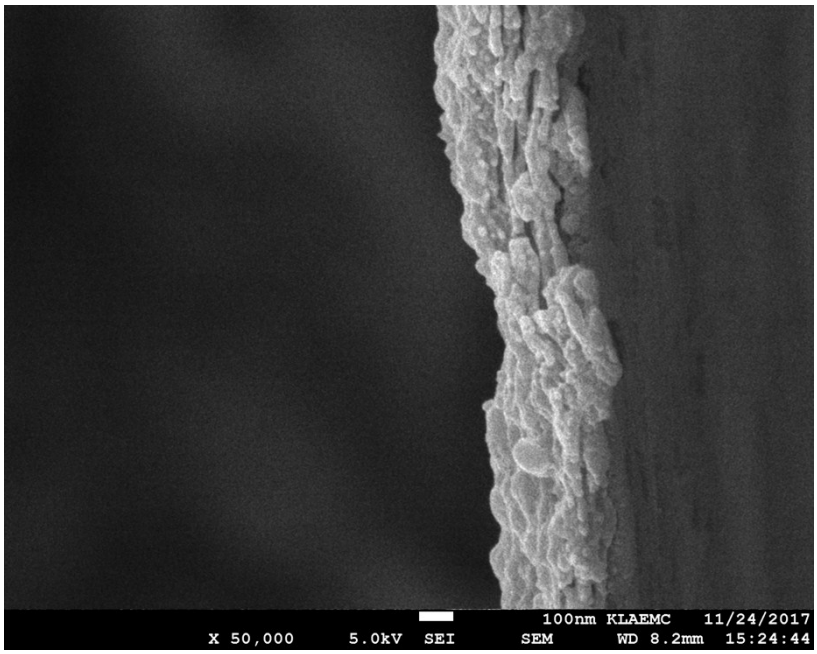

Figure S9. SEM images of the expanded edge of pTC-P5A film. SEM samples were prepared by pipette a small piece of films stored in EtOH solution with plastic dropper and dropped on wafer.

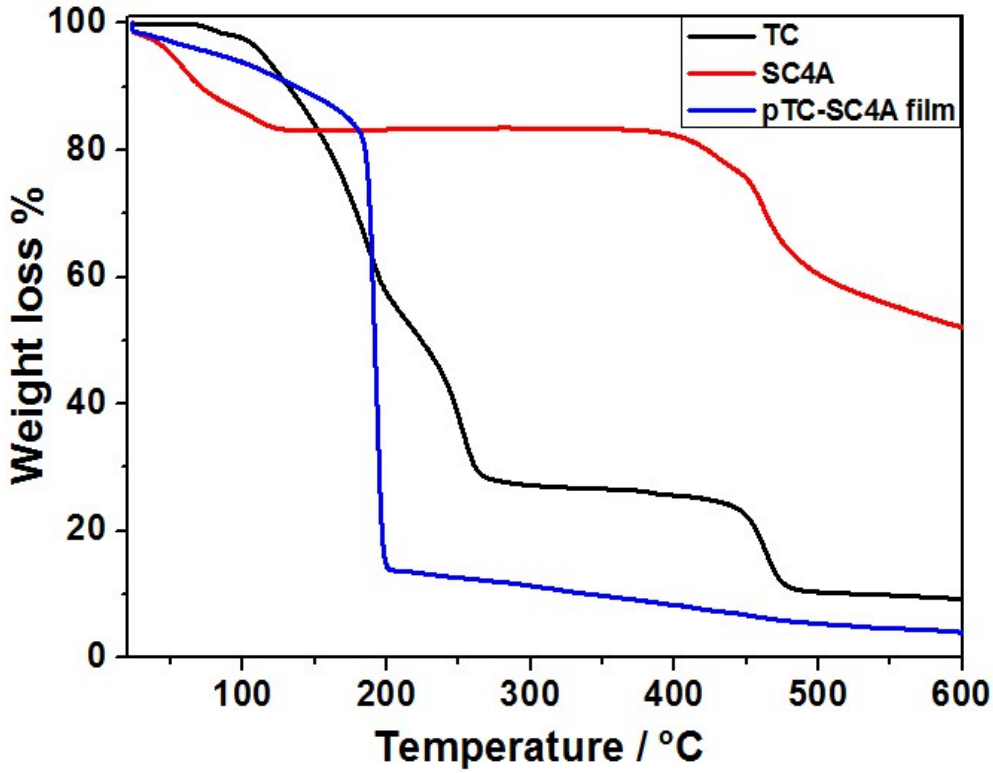

Figure S10. TGA curves for SC4A (red), pTC-SC4A film (blue), TC (black).

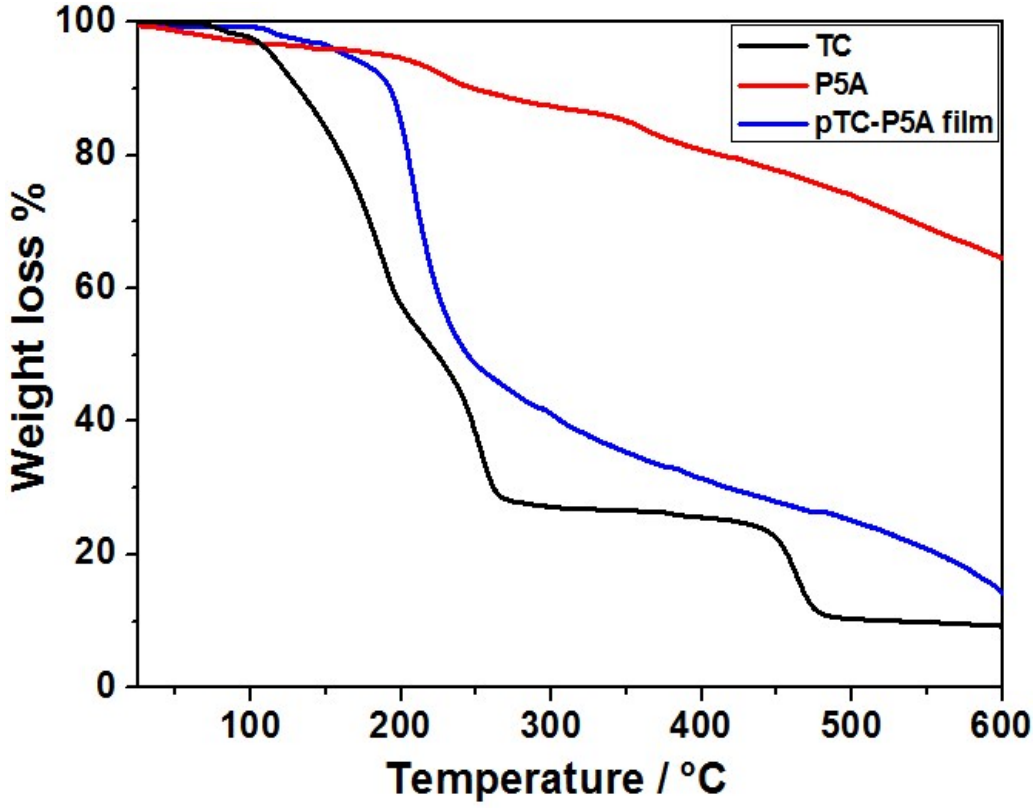

Figure S11. TGA curves for P5A (red), pTC-P5A film (blue), TC (black).

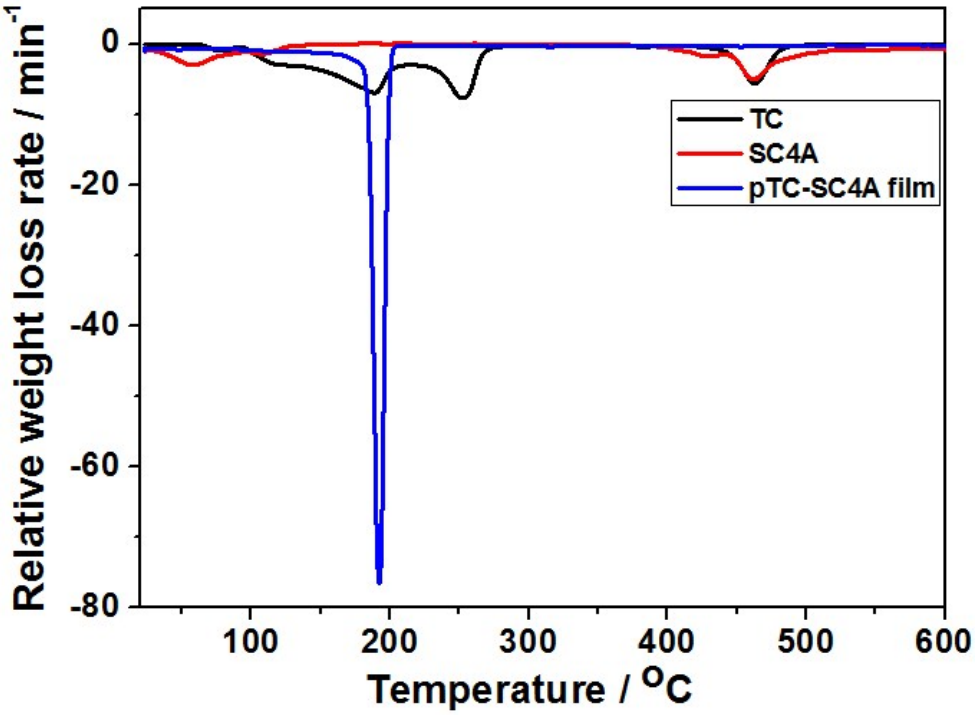

Figure S12. Relative weight loss rate curves for SC4A(red), pTC-SC4A film(blue), TC(black).

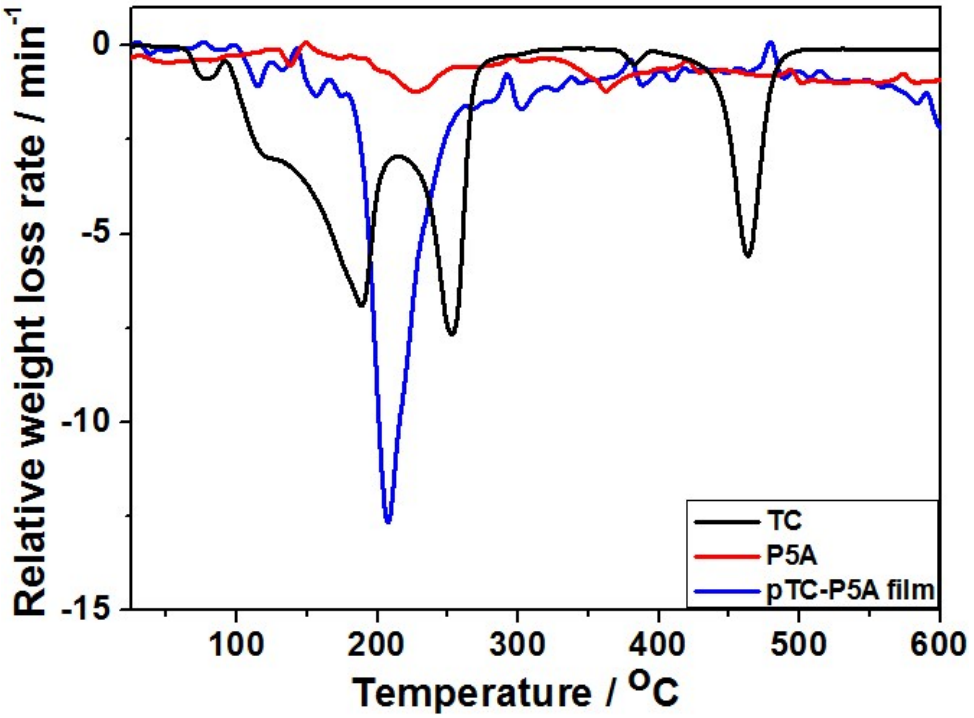

Figure S13. Relative weight loss rate curves for P5A(red), pTC-P5A film(blue), TC(black).

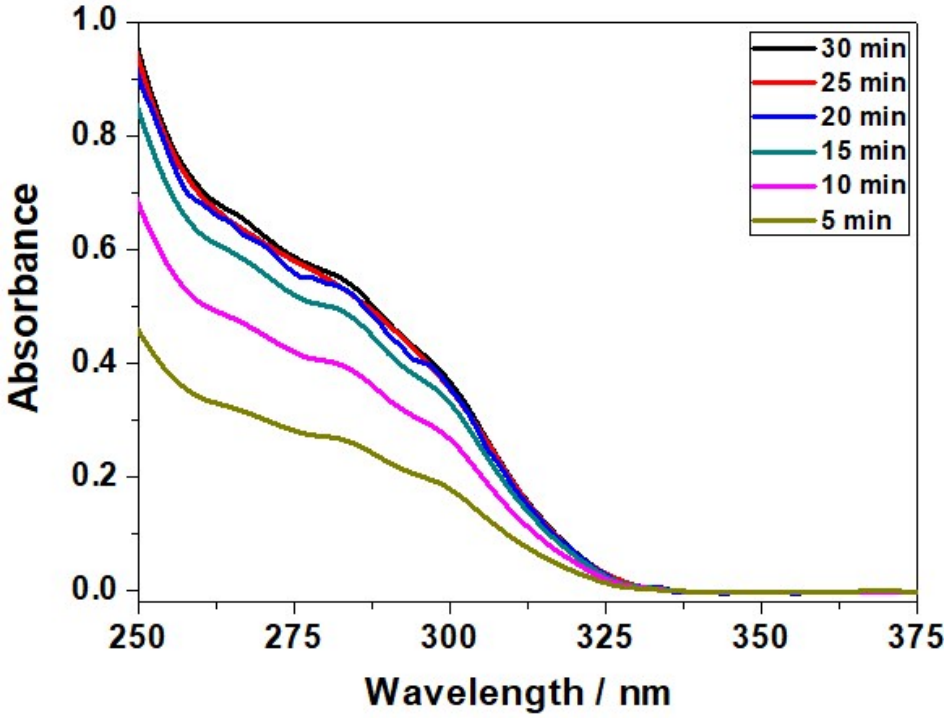

Figure S14. UV-Vis spectra of supernatants of pTC-SC4A films at 1 mol L^{-1} NaOH aqueous solution for different time (2 mg pTC-SC4A films in 10 mL alkaline aqueous solution).

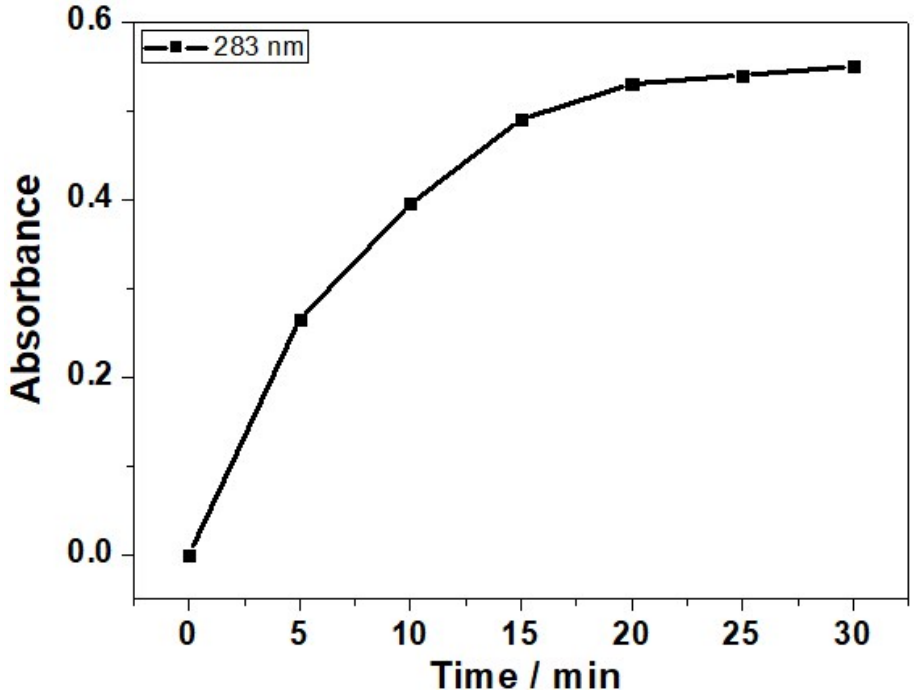

Figure S15. UV-Vis absorbance of supernatants (pH =14) of pTC-SC4A films at 283 nm. The films could be totally hydrolyzed in 30 minutes.

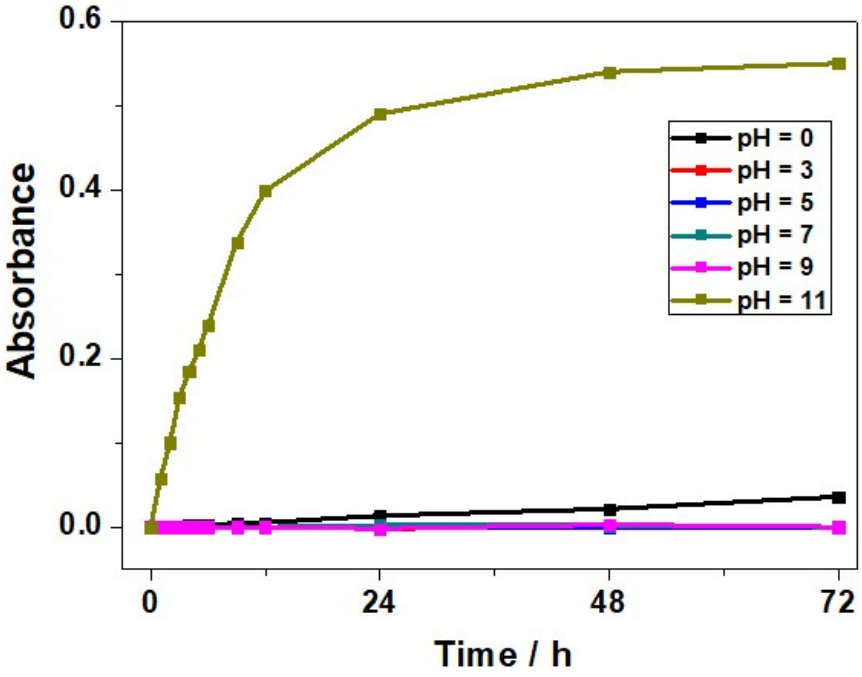

Figure S16. UV-Vis absorbance of supernatants of pTC-SC4A films with different pH at 283 nm (2 mg pTC-SC4A films in 10 mL acidic or alkaline aqueous solution). At pH = 11, the films could totally decomposed after 3 days; at pH = 0, the films decomposed gradually less than 20 % in 3 days; at pH 3-9, the films could keep stable for at least 3 days.

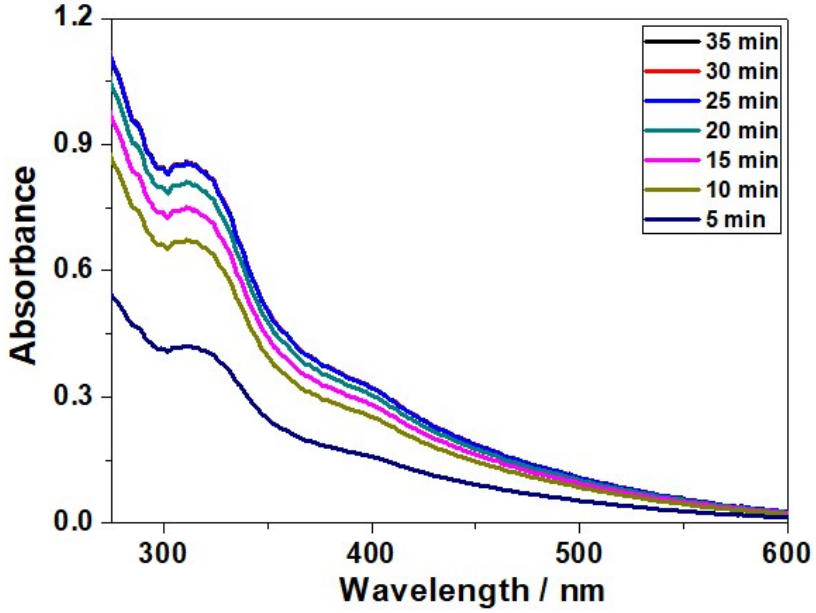

Figure S17. UV-Vis spectra of supernatants of pTC-P5A films at 1 mol L^{-1} NaOH aqueous solution for different time (2 mg pTC-P5A films in 10 mL alkaline aqueous solution).

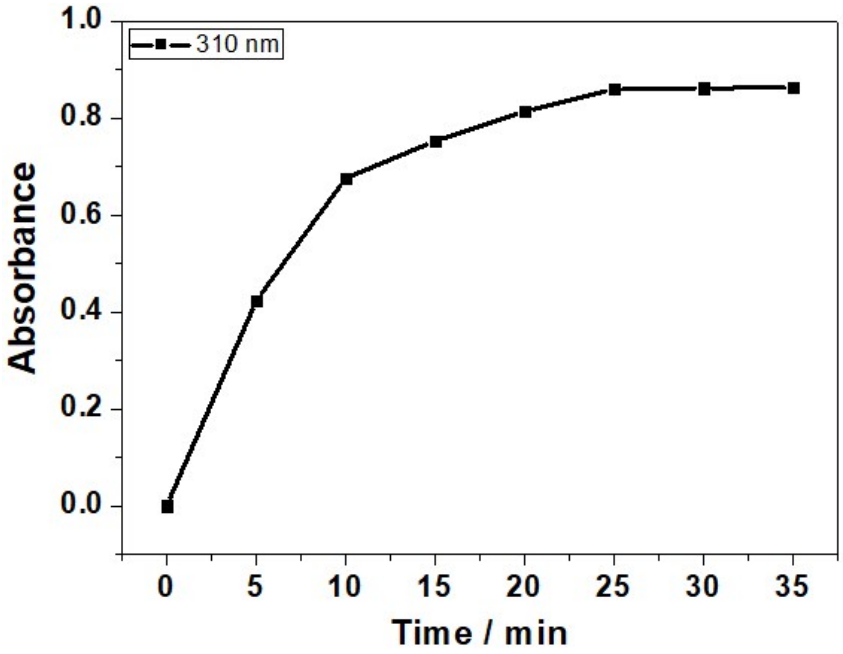

Figure S18. UV-Vis absorbance of supernatants (pH =14) of pTC-P5A films at 310 nm. The films could be totally hydrolyzed in 30 minutes.

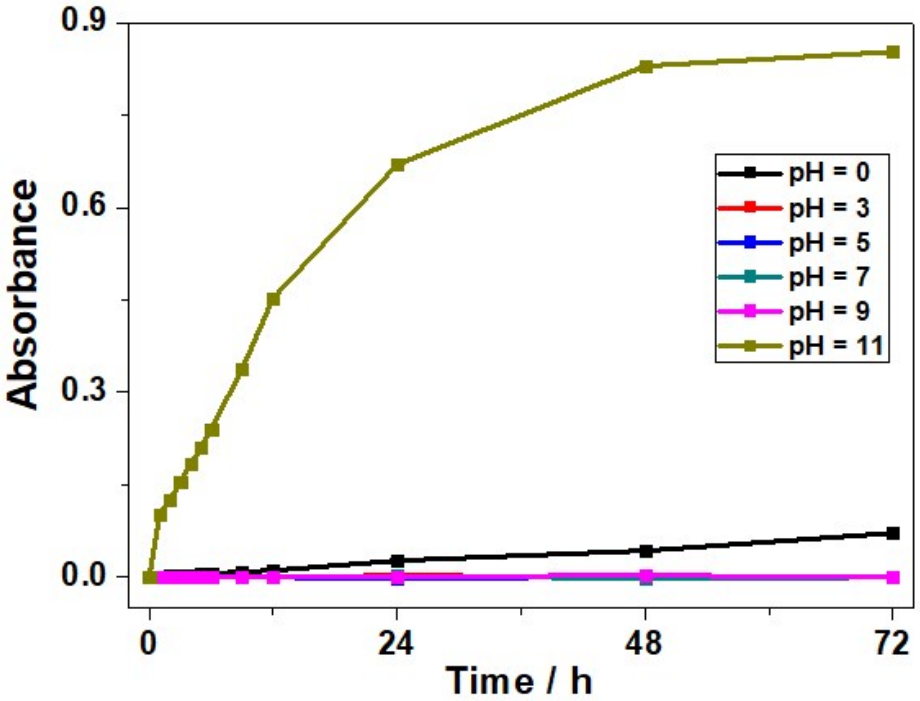

Figure S19. UV-Vis absorbance of supernatants of pTC-P5A films with different pH at 310 nm (2 mg pTC-P5A films in 10 mL acidic or alkaline aqueous solution). At pH = 11, the films could totally decomposed after 3 days; at pH = 0, the films decomposed gradually less than 20 % in 3 days; at pH 3-9, the films could keep stable for at least 3 days.

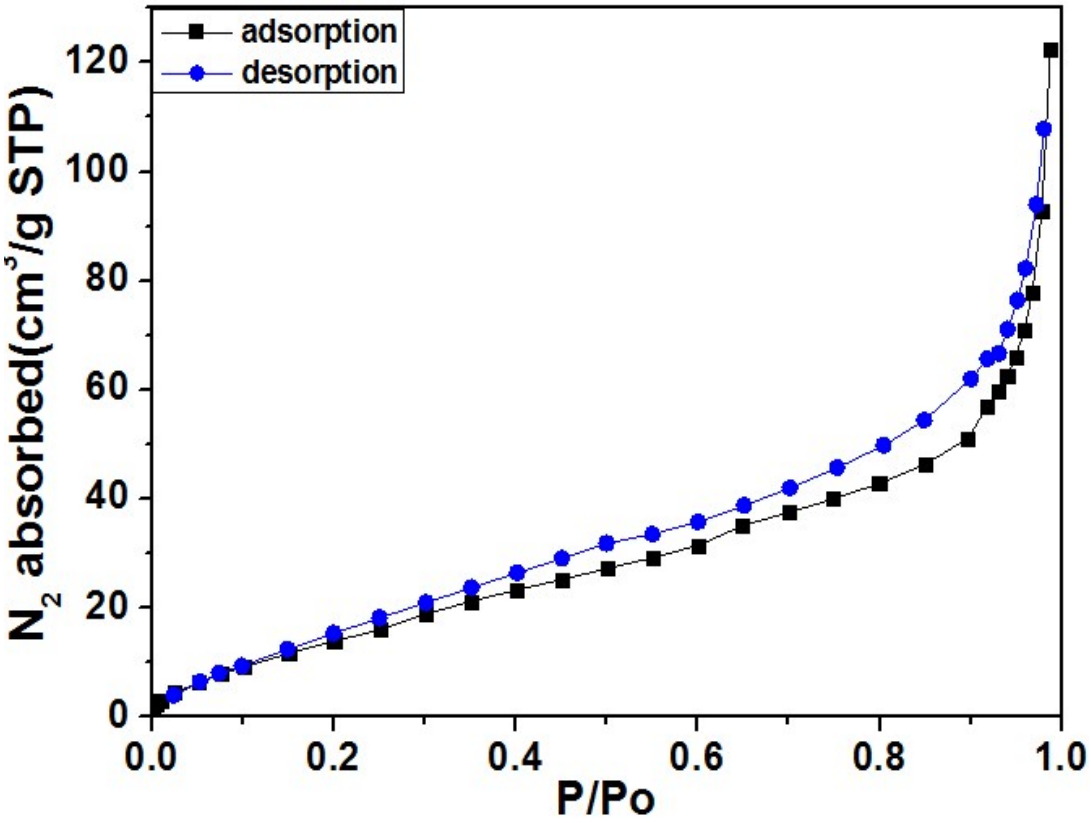

Figure S20. N_2 adsorption (blue squares) and desorption (grey squares) isotherms of pTC-SC4A film. The solid line is a guide to the eye. S_{BET} is the Brunauer–Emmett–Teller (BET) surface area (in units of $m^2\ g^{-1}$) of pTC-SC4A film calculated from the N_2 adsorption isotherm, and P and P_0 are the equilibrium and saturation pressures of N_2 at 77 K, respectively. To obtain enough material for the analysis, we isolated pTC-SC4A films from 100 pieces of supports prepared at the optimal condition.

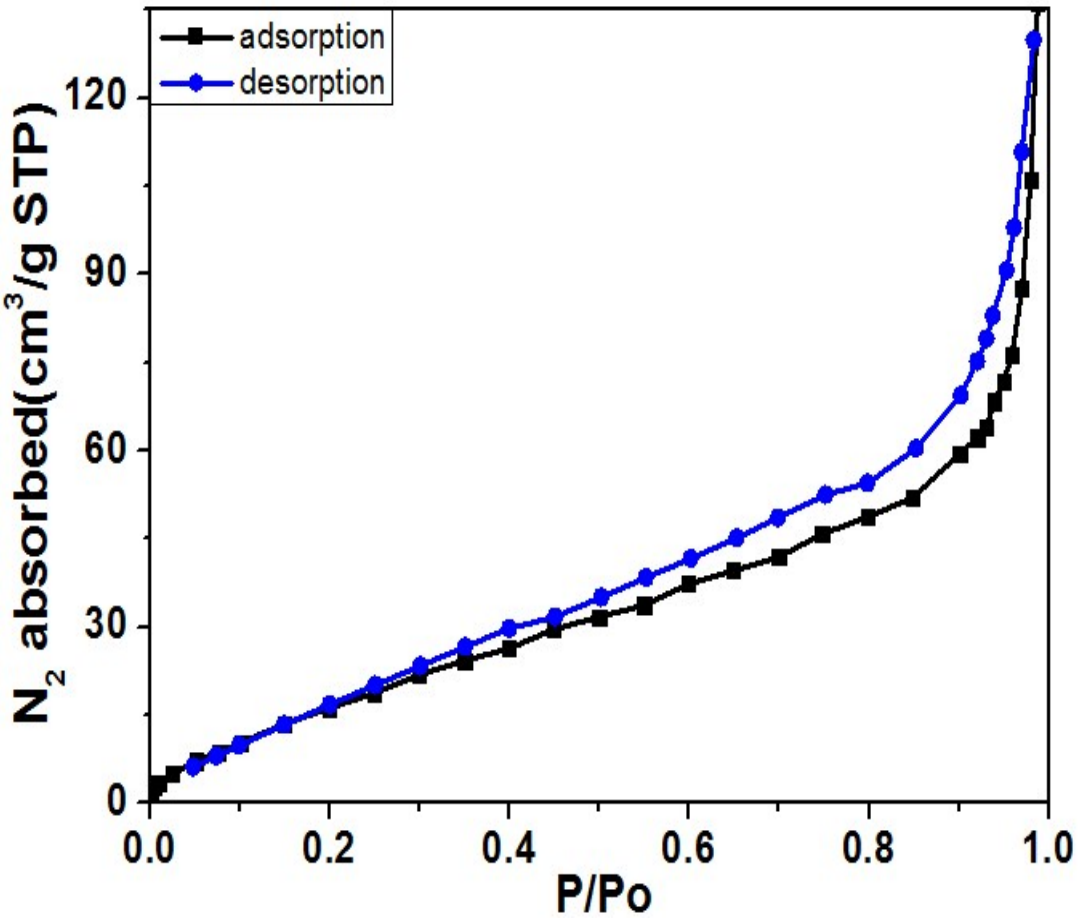

Figure S21. N_2 adsorption (blue squares) and desorption (grey squares) isotherms of pTC-P5A film. The solid line is a guide to the eye. S_{BET} is the Brunauer–Emmett–Teller (BET) surface area (in units of $m^2\ g^{-1}$) of pTC-P5A film or pTC-P5A film calculated from the N_2 adsorption isotherm, and P and P_0 are the equilibrium and saturation pressures of N_2 at 77 K, respectively. To obtain enough material for the analysis, we isolated pTC-SC4A films from 100 pieces of supports prepared at the optimal condition.

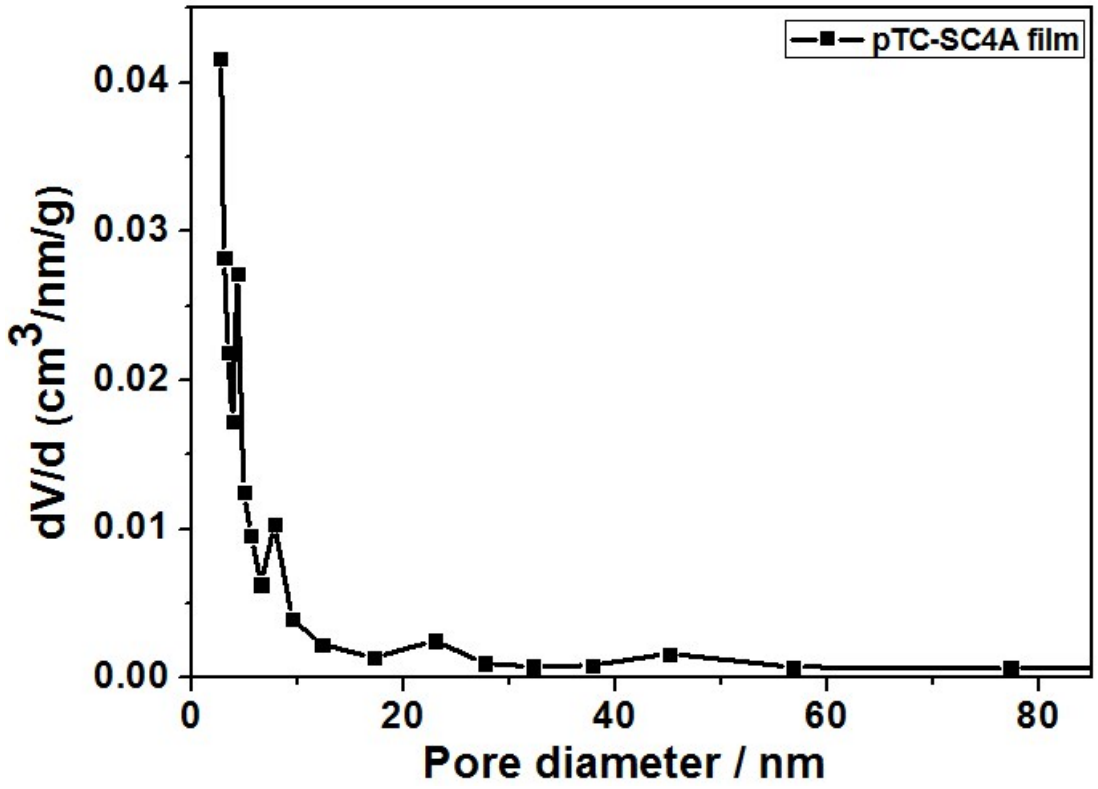

Figure S22. Distribution of surface area along with pore diameter of pTC-SC4A film obtained by NLDFT analysis. To obtain enough material for the analysis, we isolated pTC-SC4A films from 100 pieces of supports prepared at their optimal conditions respectively.

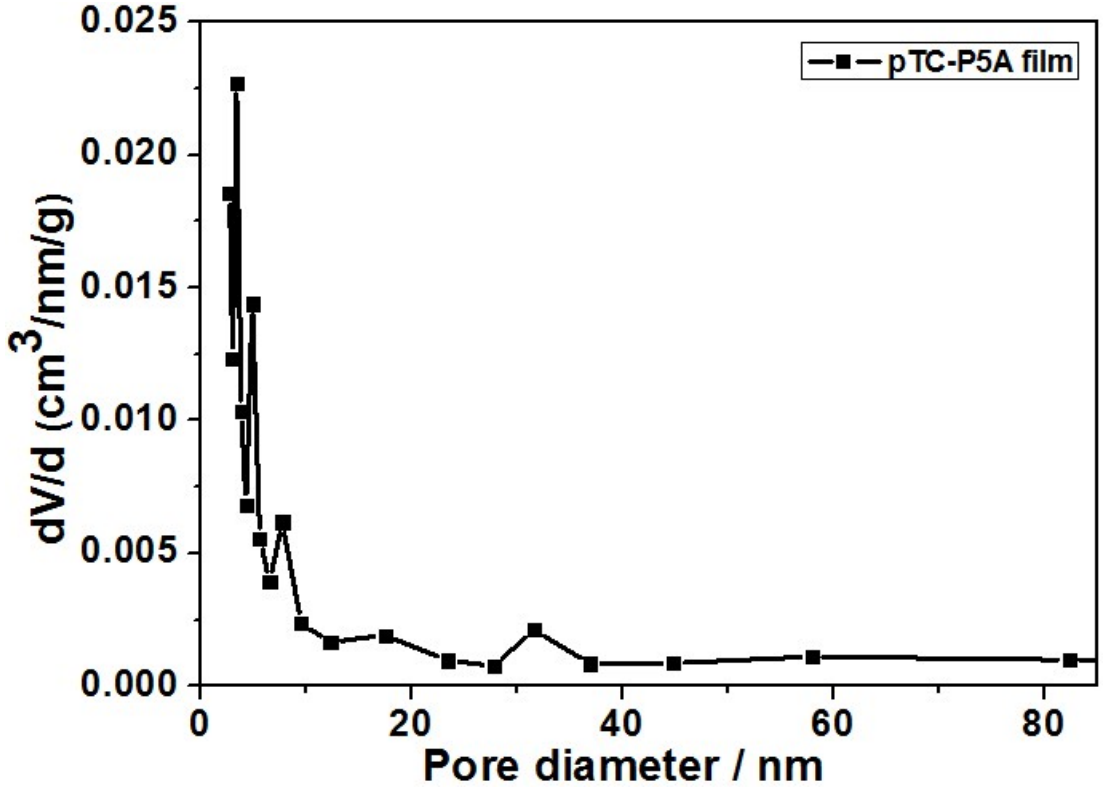

Figure S23. Distribution of surface area along with pore diameter of pTC-P5A film obtained by NLDFT analysis. To obtain enough material for the analysis, we isolated pTC-P5A films from 100 pieces of supports prepared at their optimal conditions respectively.

5. Filter performance determined by UV/Vis spectroscopy.

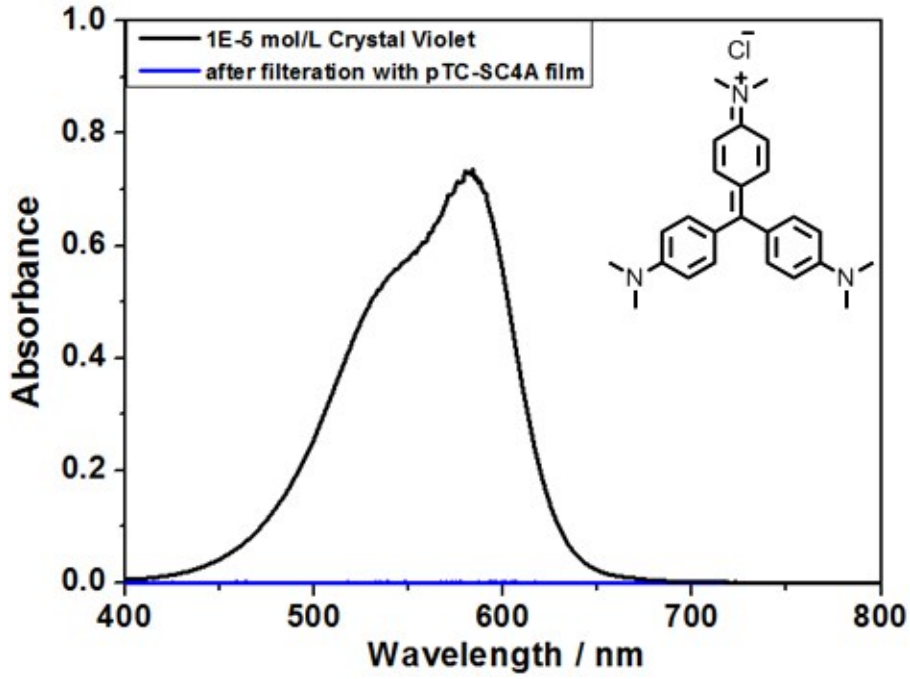

Figure S24a. **UV-Vis spectra of crystal violet before and after filtration with pTC-SC4A film** (Insert: the structure of crystal violet).

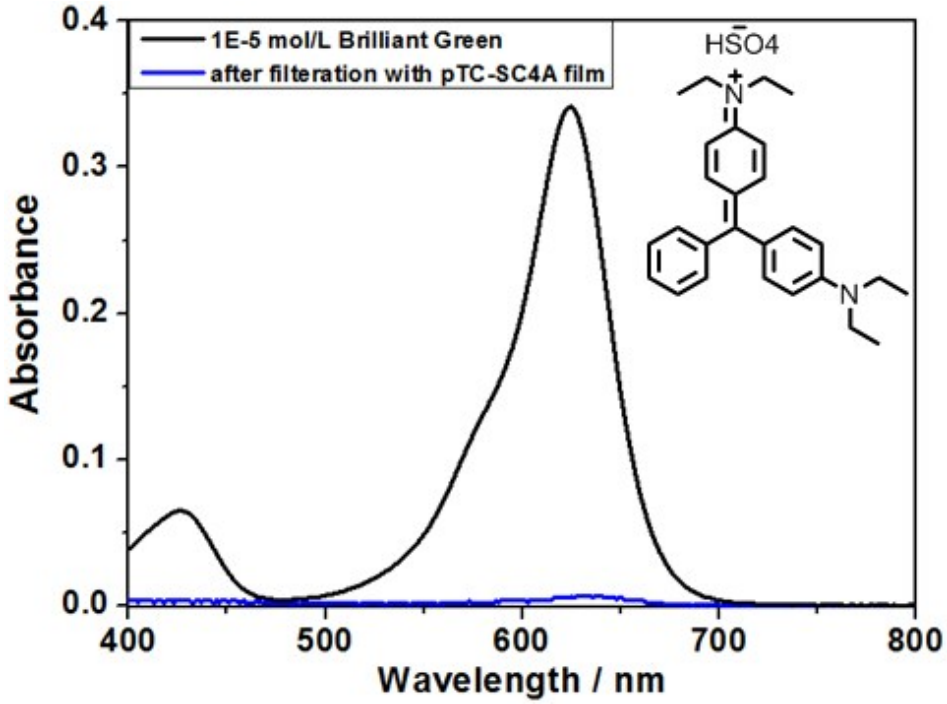

Figure S24b. UV-Vis spectra of brilliant green before and after filtration with pTC-SC4A film (Insert : the structure of brilliant green).

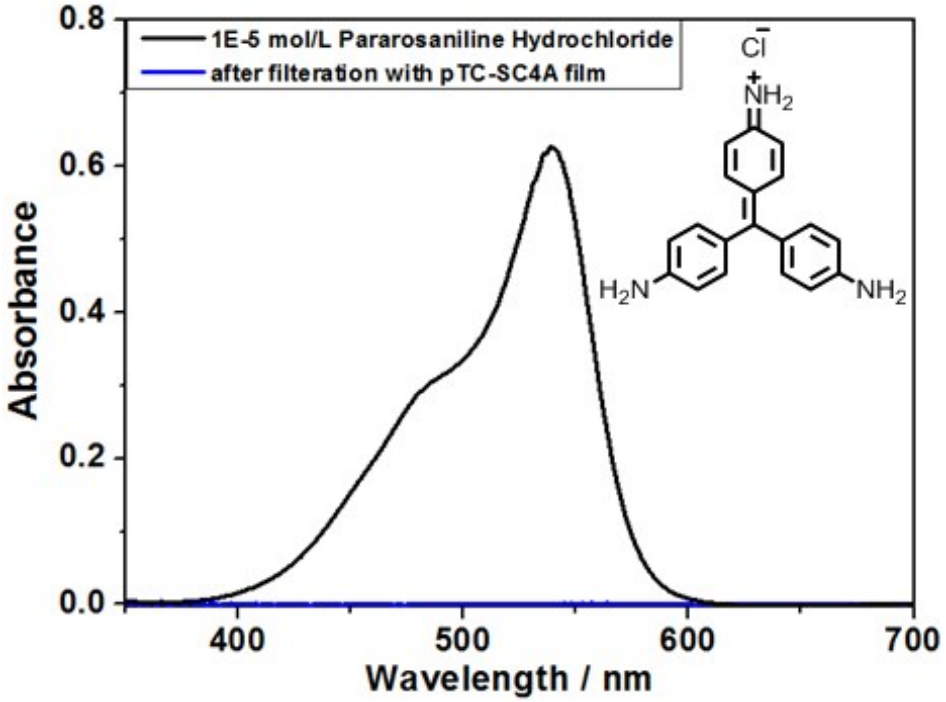

Figure S24c. UV-Vis spectra of pararosaniline hydrochloride before and after filtration with pTC-SC4A film (Insert: the structure of pararosaniline hydrochloride).

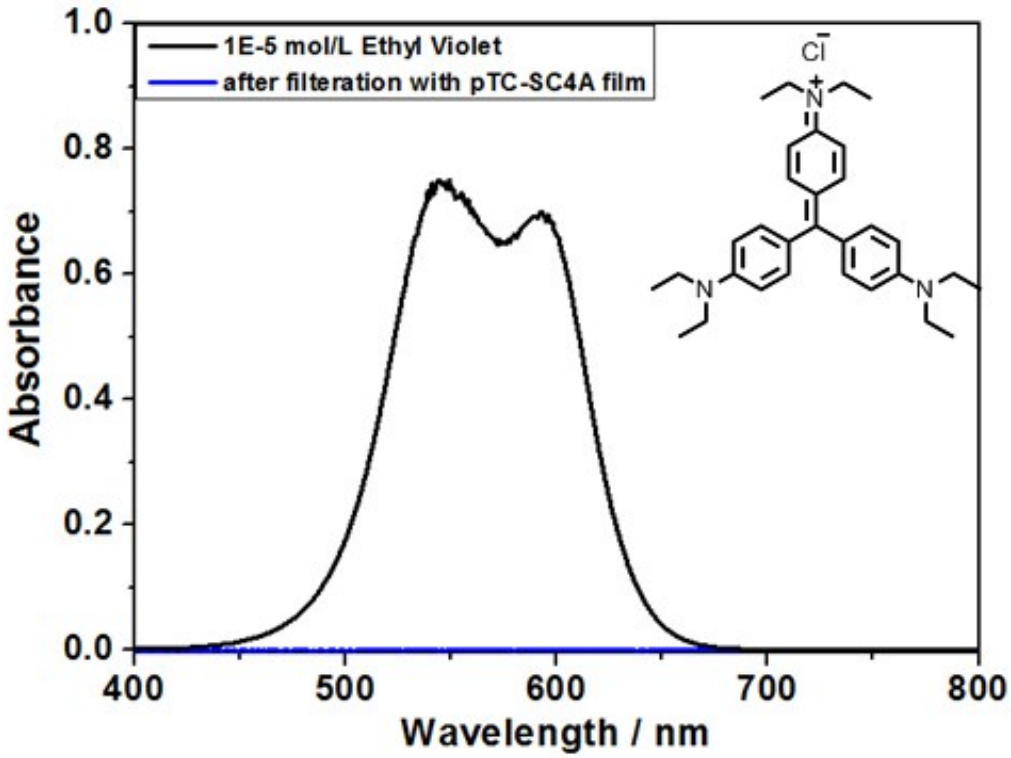

Figure S24d. UV-Vis spectra of ethyl violet before and after filtration with pTC-SC4A film (Insert: the structure of ethyl violet).

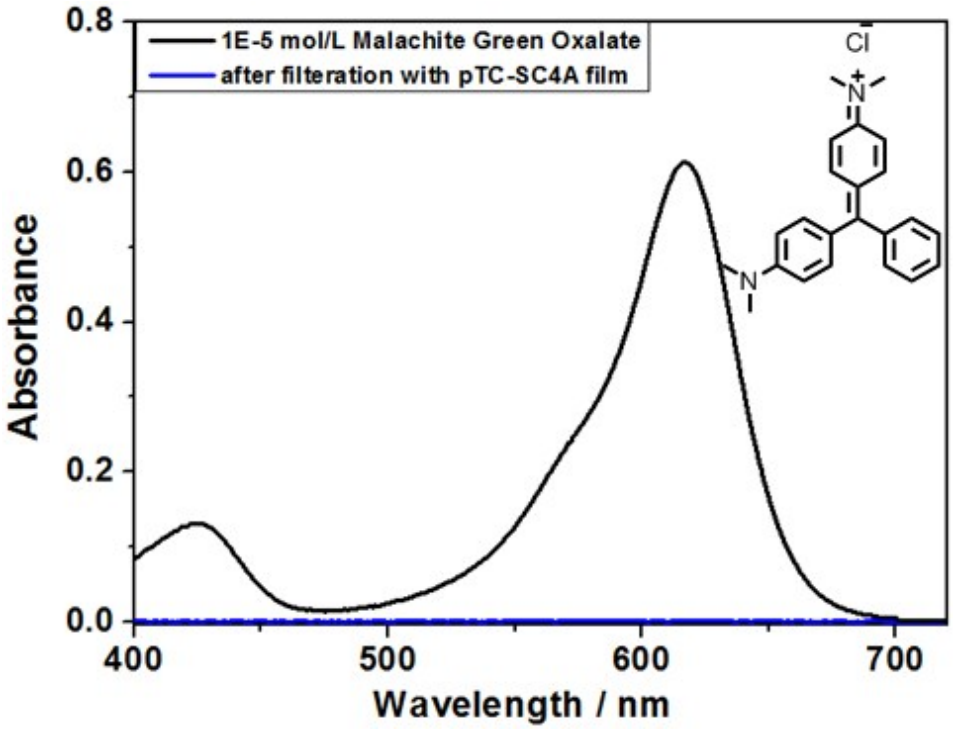

Figure S24e. UV-Vis spectra of malachite green oxalate before and after filtration with pTC-SC4A film (Insert: the structure of malachite green oxalate).

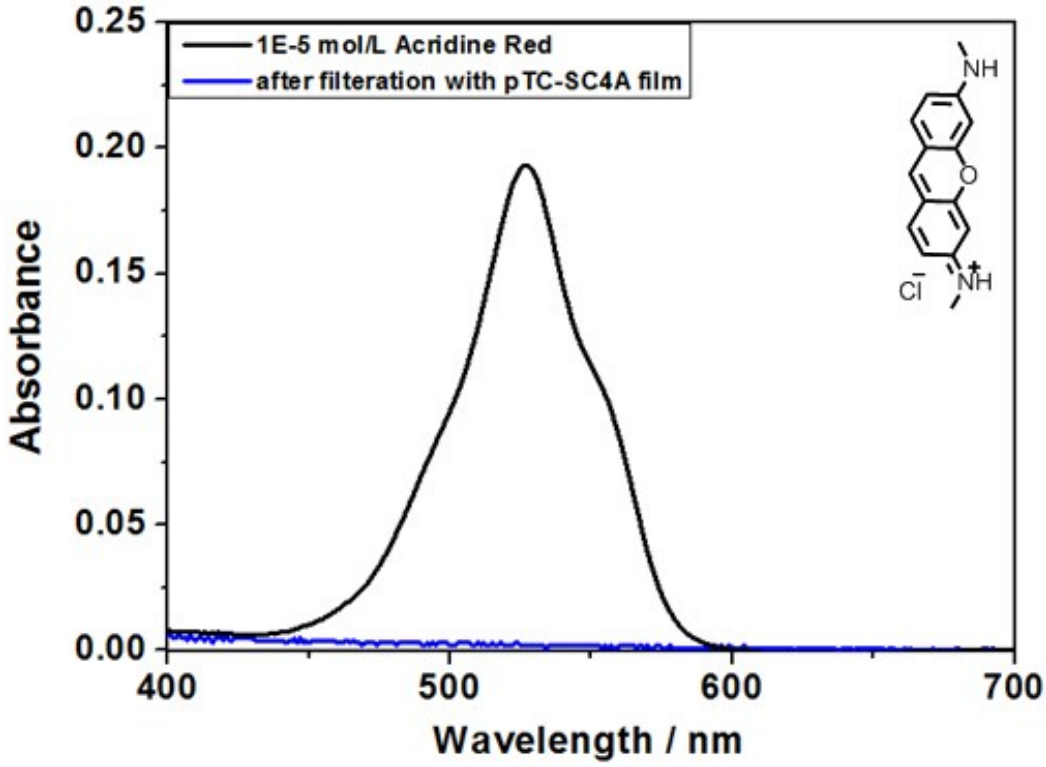

Figure S24f. UV-Vis spectra of acridine red before and after filtration with pTC-SC4A film (Insert: the structure of acridine red).

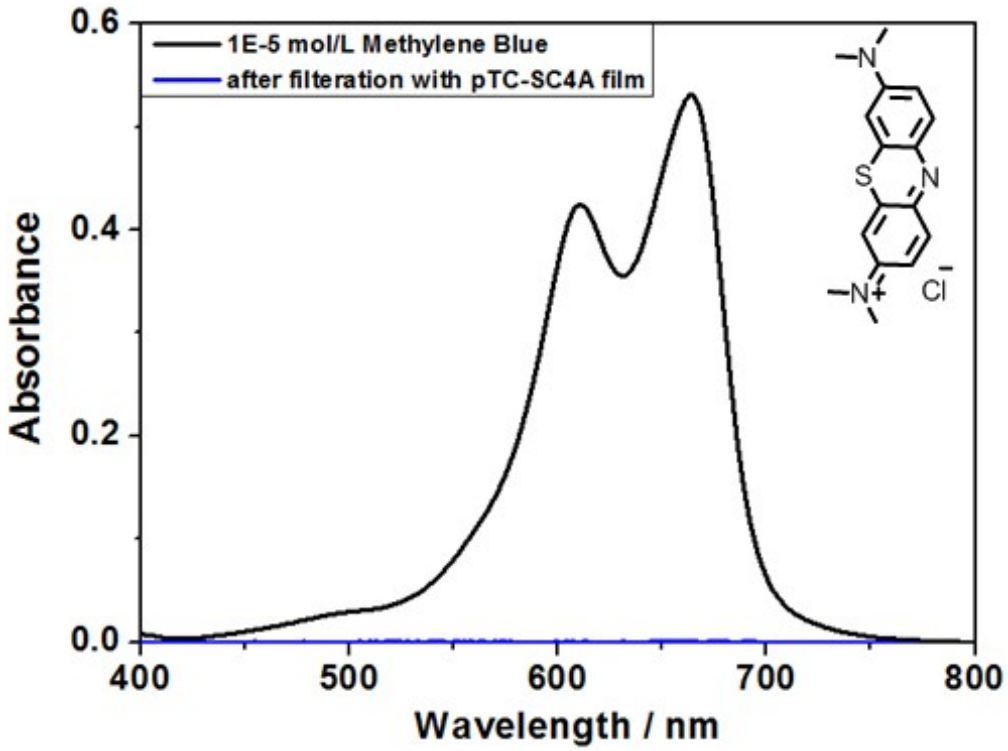

Figure S24g. UV-Vis spectra of methylene blue before and after filtration with pTC-SC4A film (Insert: the structure of methylene blue).

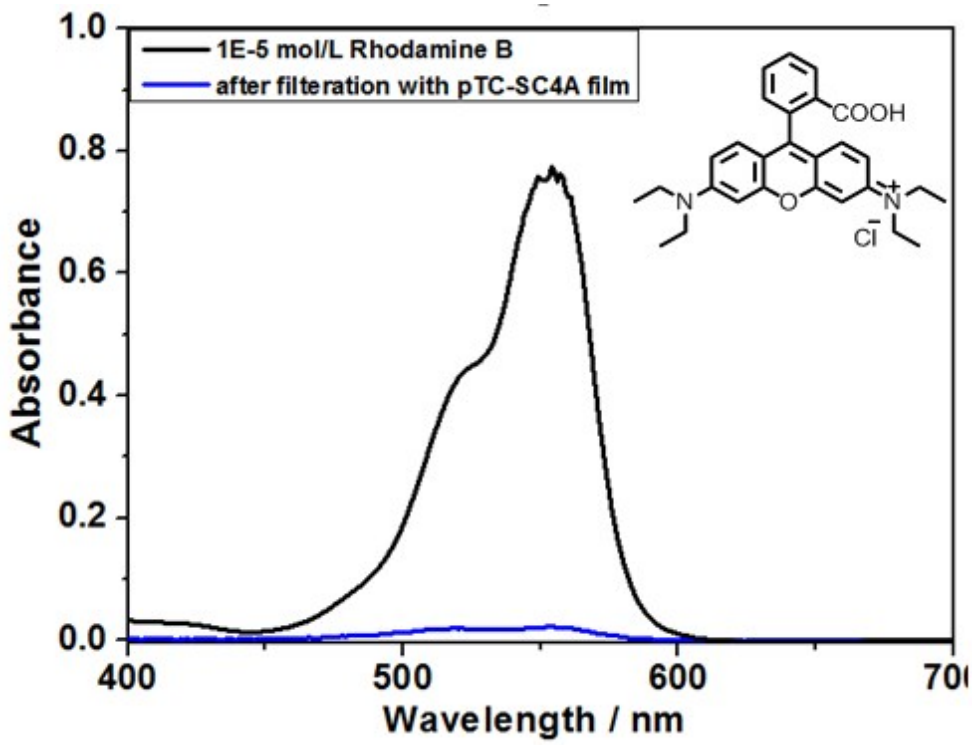

Figure S24h. UV-Vis spectra of rhodamine B before and after filtration with pTC-SC4A film (Insert : the structure of rhodamine B).

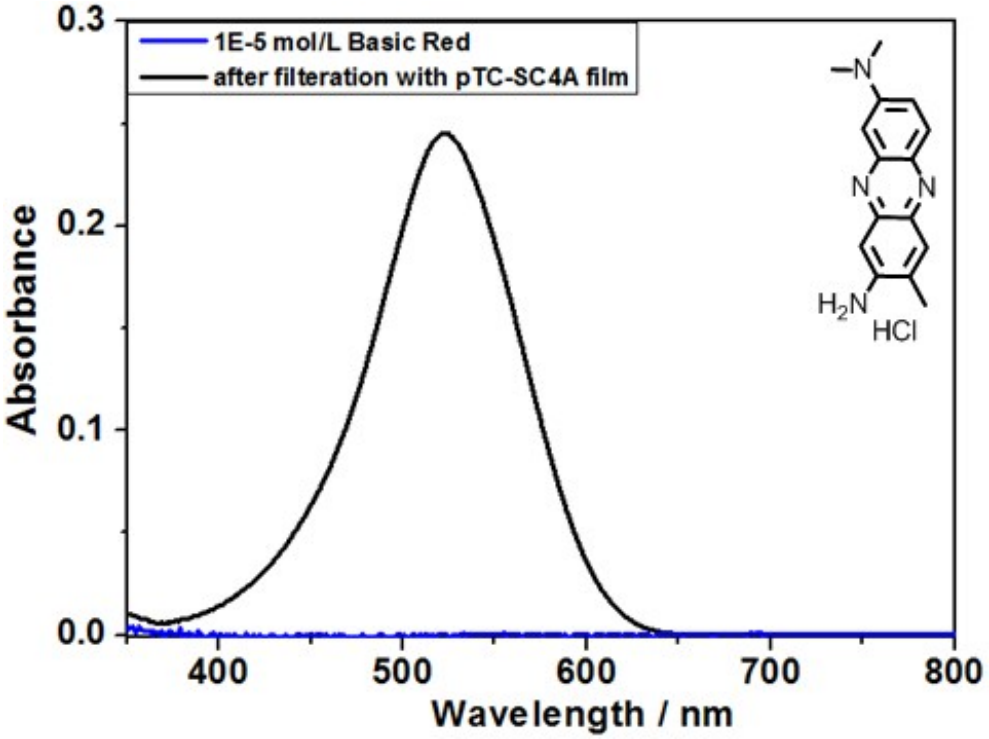

Figure S24i. UV-Vis spectra of basic red before and after filtration with pTC-SC4A film (Insert: the structure of basic red).

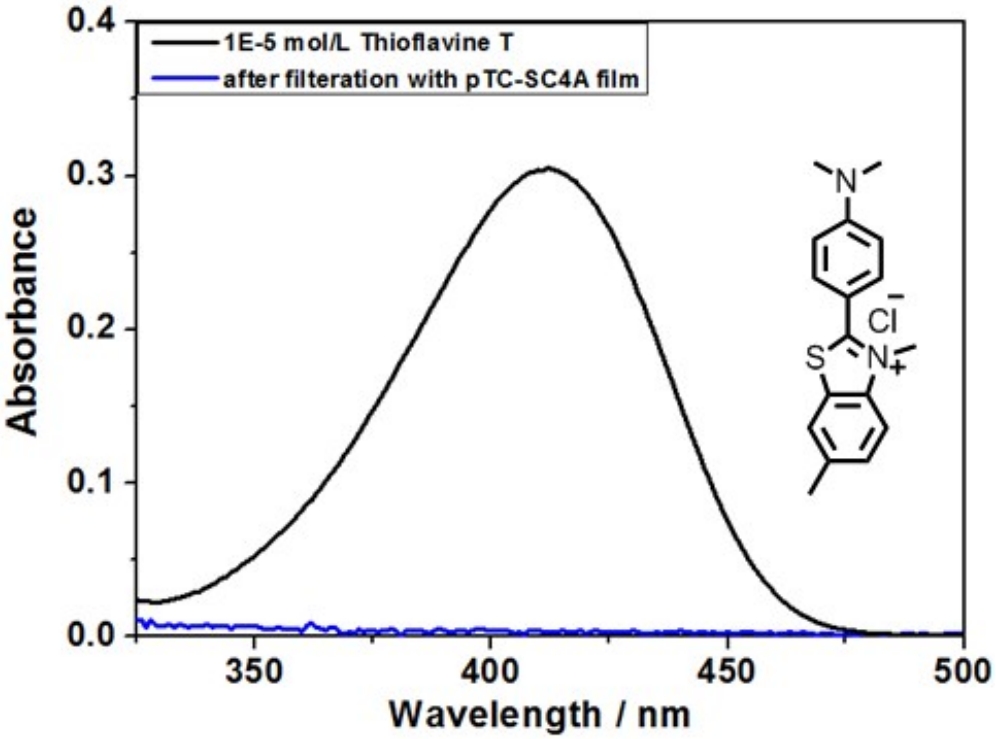

Figure S24j. UV-Vis spectra of thioflavine T before and after filtration with pTC-SC4A film (Insert : the structure of thioflavine T).

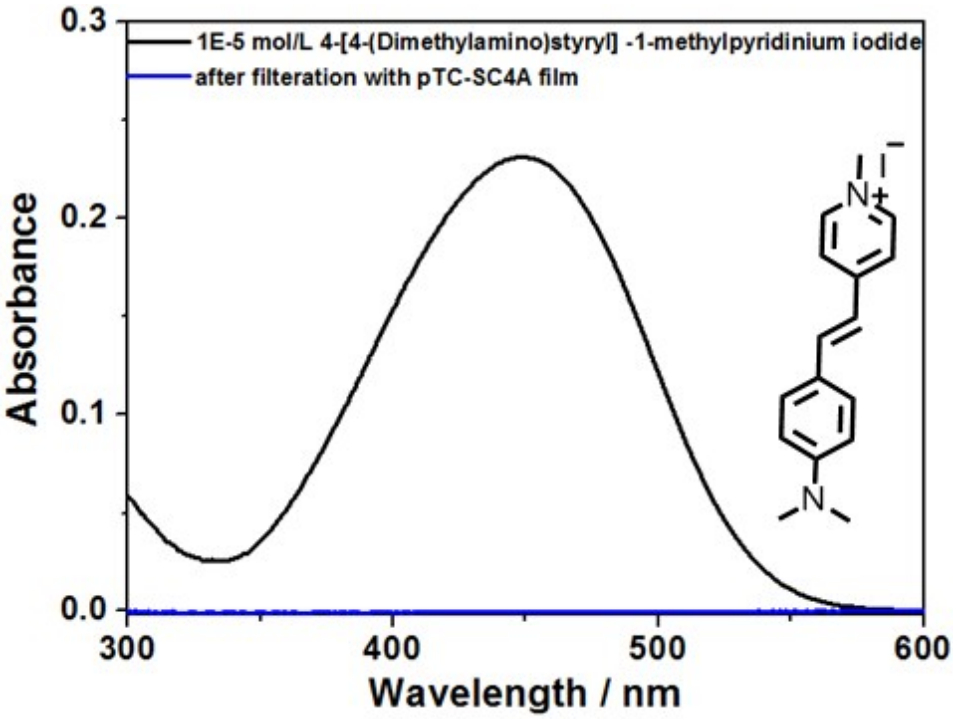

Figure S24k. **UV-Vis spectra of 4-[4-(dimethyamino)styryl]-1-methylpyridinium iodide before and after filtration with pTC-SC4A film** (Insert: the structure of 4-[4-(dimethyamino)styryl]-1-methylpyridinium iodide).

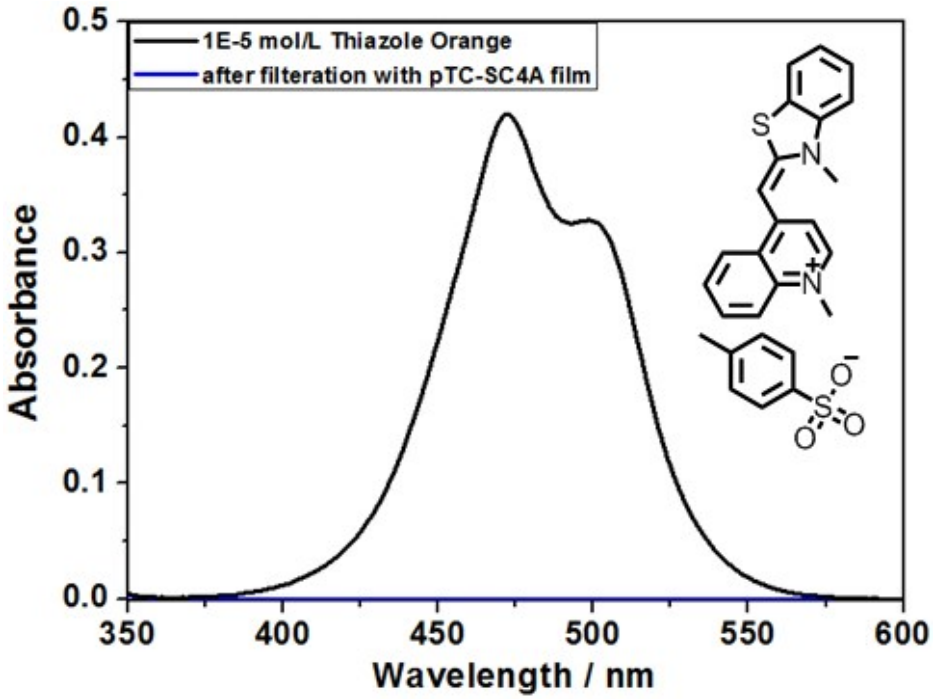

Figure S24l. UV-Vis spectra of thiazole orange before and after filtration with pTC-SC4A film (Insert: the structure of thiazole orange).

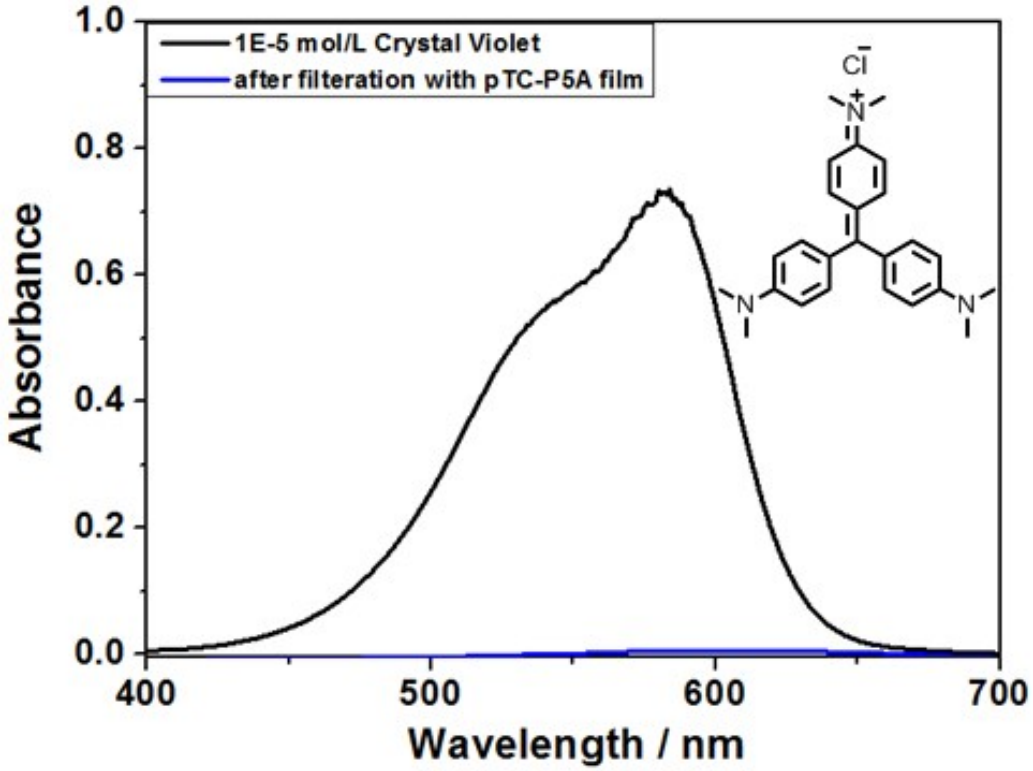

Figure S25a. UV-Vis spectra of crystal violet before and after filtration with pTC-P5A film (Insert: the structure of crystal violet).

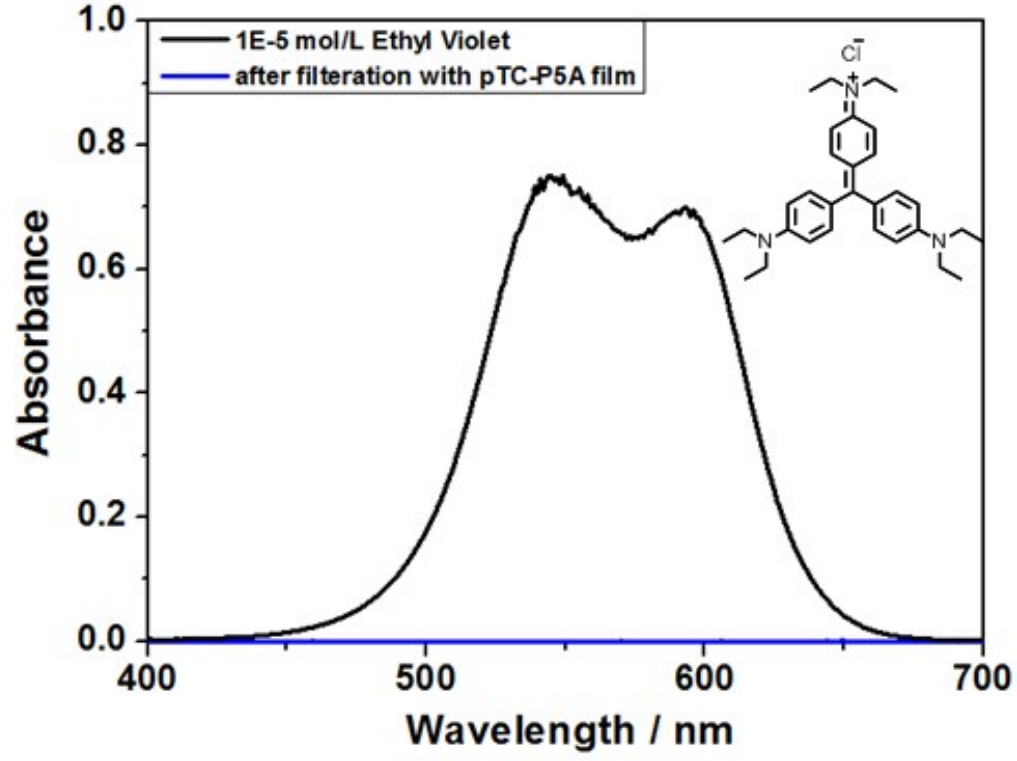

Figure S25b. UV-Vis spectra of ethyl violet before and after filtration with pTC-P5A film (Insert: the structure of ethyl violet).

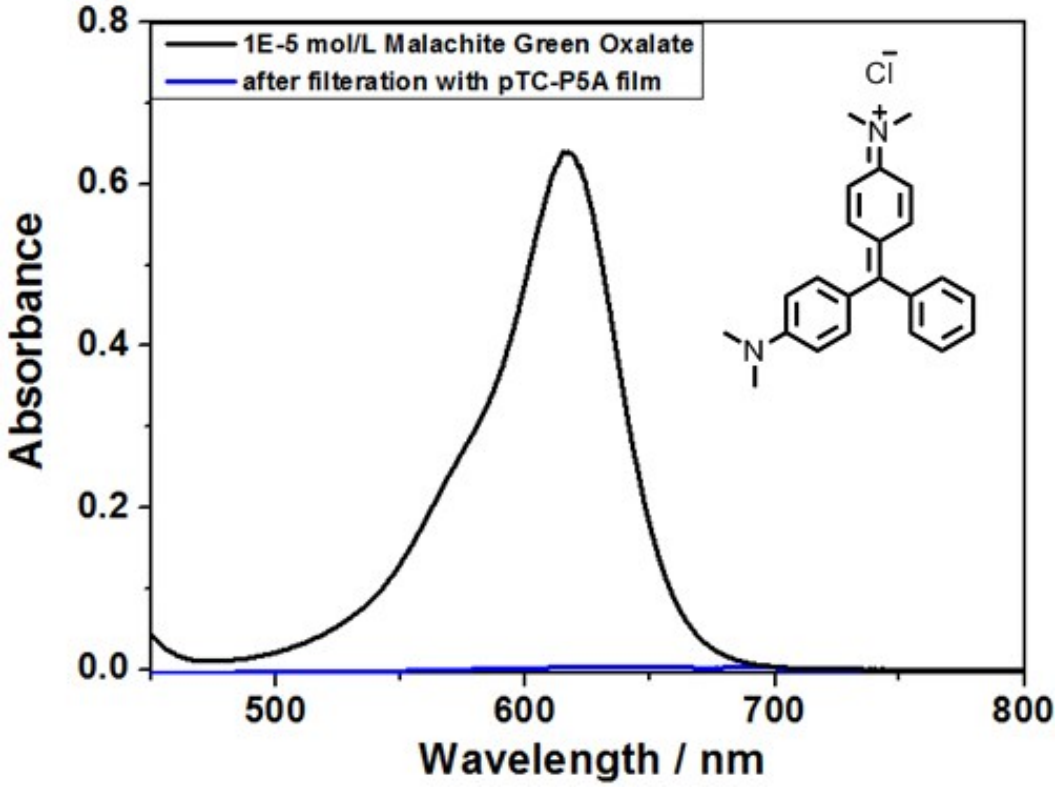

Figure S25c. UV-Vis spectra of malachite green oxalate before and after filtration with pTC-P5A film (Insert: the structure of malachite green oxalate).

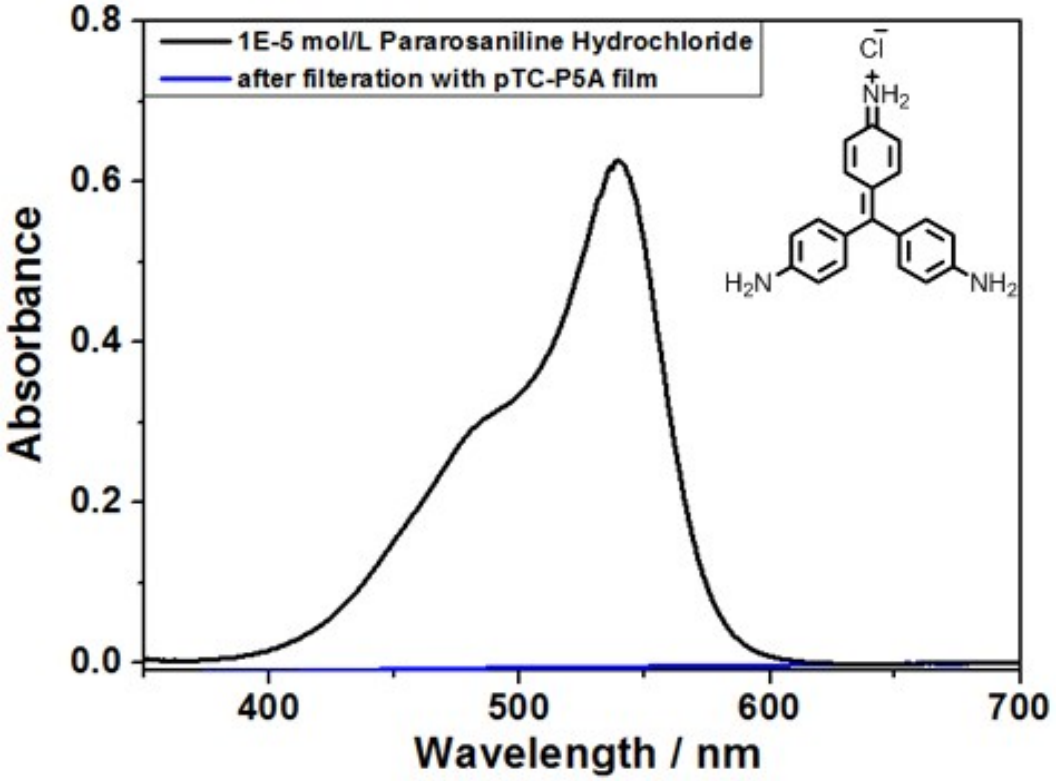

Figure S25d. UV-Vis spectra of pararosaniline hydrochloride before and after filtration with pTC-P5A film (Insert: the structure of pararosaniline hydrochloride).

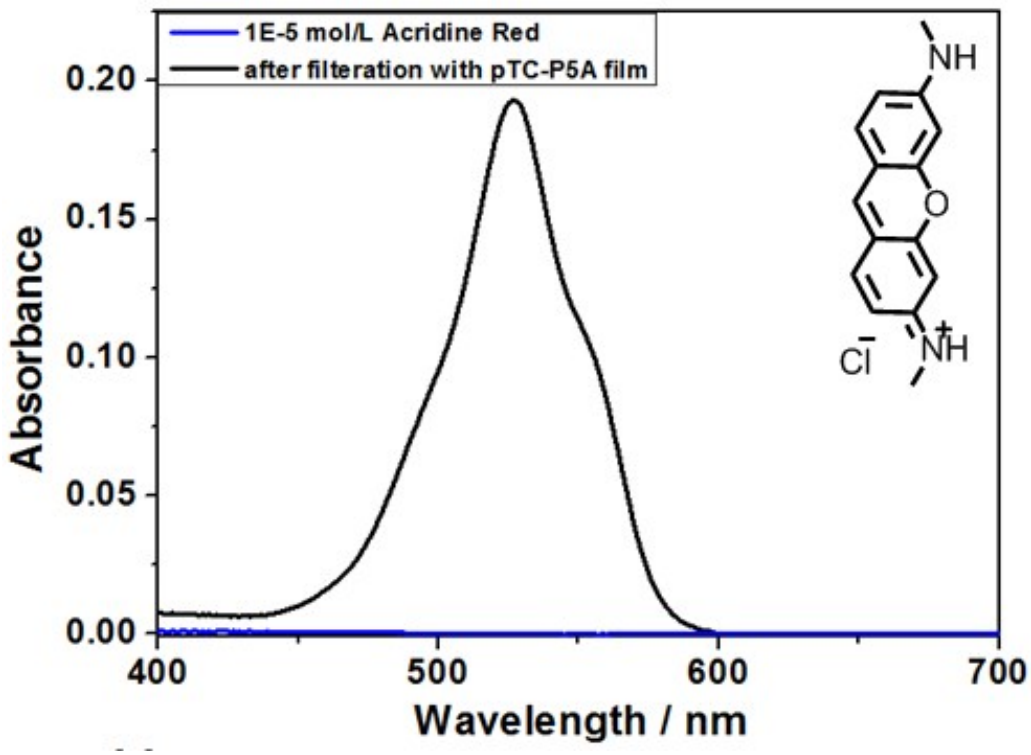

Figure S25e. UV-Vis spectra of acridine red before and after filtration with pTC-P5A film (Insert: the structure of acridine red).

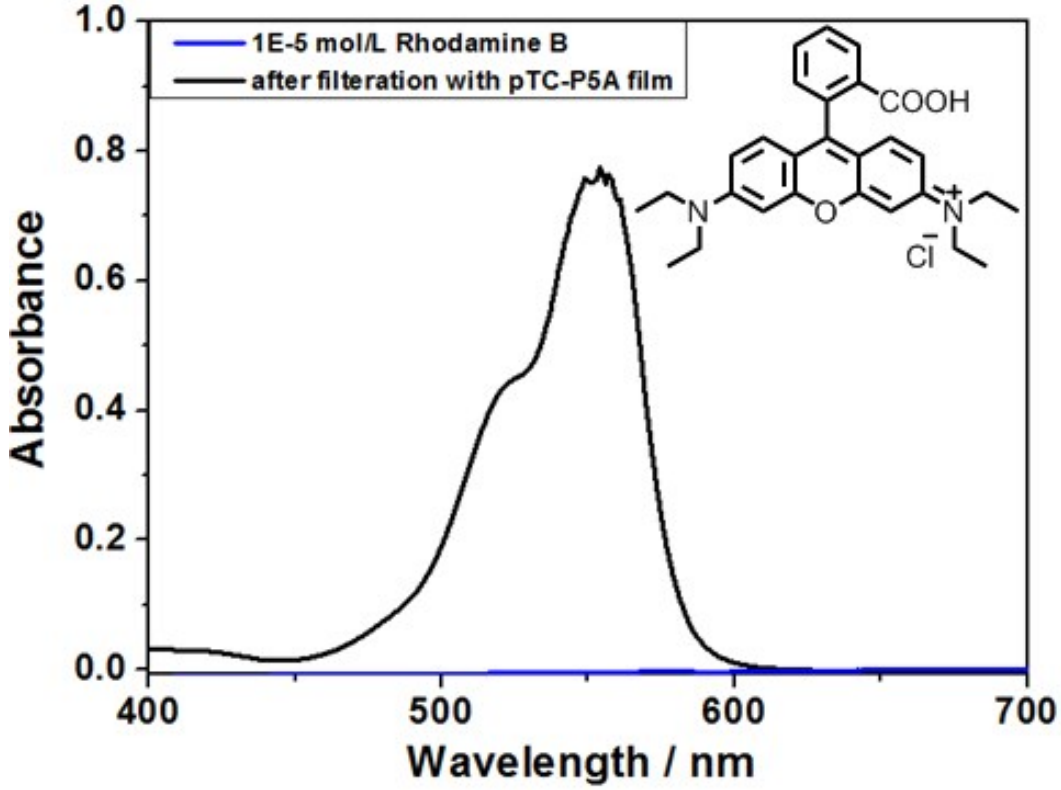

Figure S25f. UV-Vis spectra of rhodamine B before and after filtration with pTC-P5A film (Insert: the structure of rhodamine B).

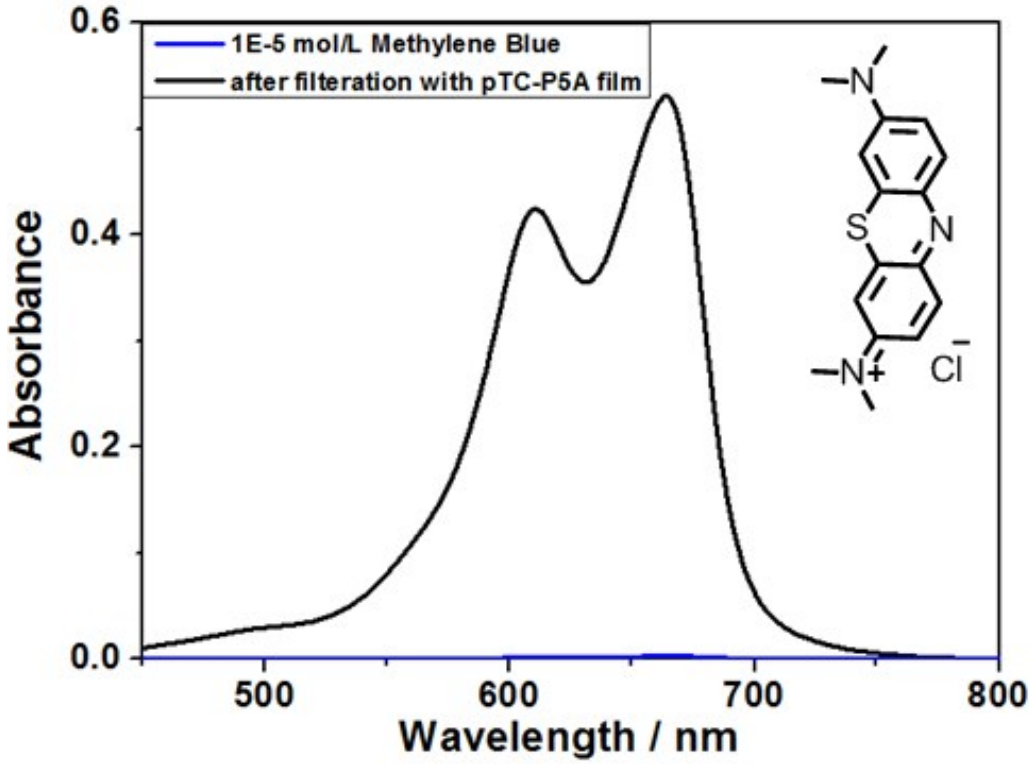

Figure S25g. UV-Vis spectra of methylene blue before and after filtration with pTC-P5A film (Insert: the structure of methylene blue).

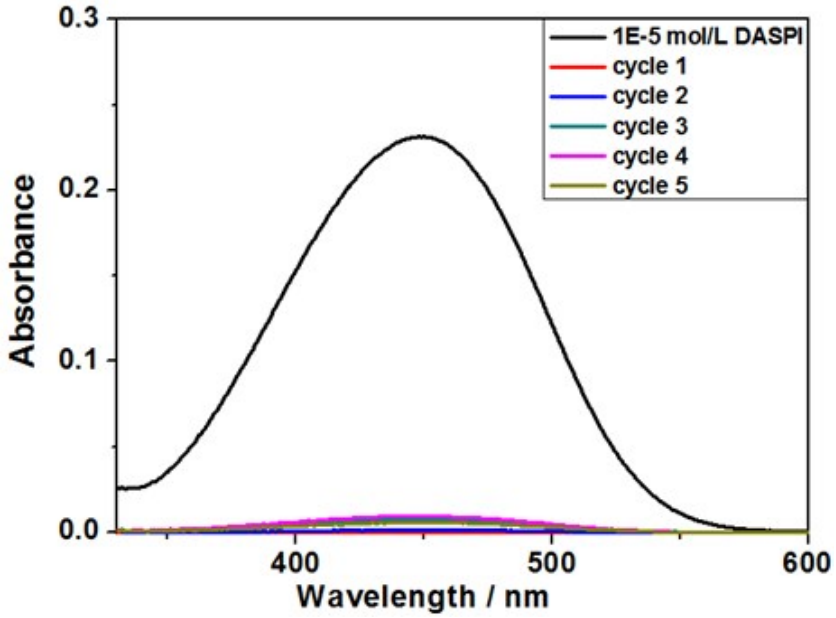

Figure S26a. UV-Vis spectra of DASPI before and after filtration with pTC-SC4A film for 5 cycles. The pTC-SC4A films could be regenerated via eluting the dyes with EtOH at room temperature by the same vacuum filtrations. Consecutive regeneration cycles were repeated for five times by using DASPI as a model compound which showed >95% removal efficiency (Figure S13).

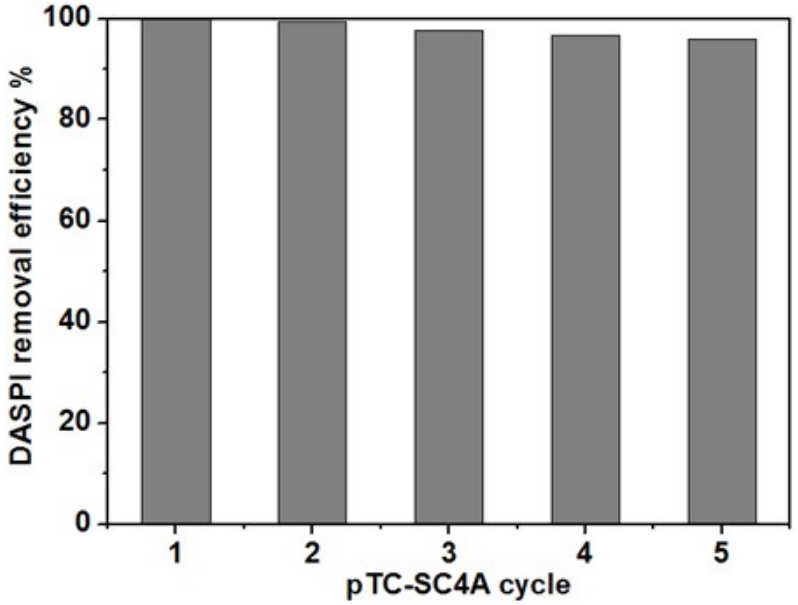

Figure S26b. Consecutive regeneration cycles were done using DASPI as model. Films were regenerated via eluting with EtOH at room temperature by the same vacuum filtrations.

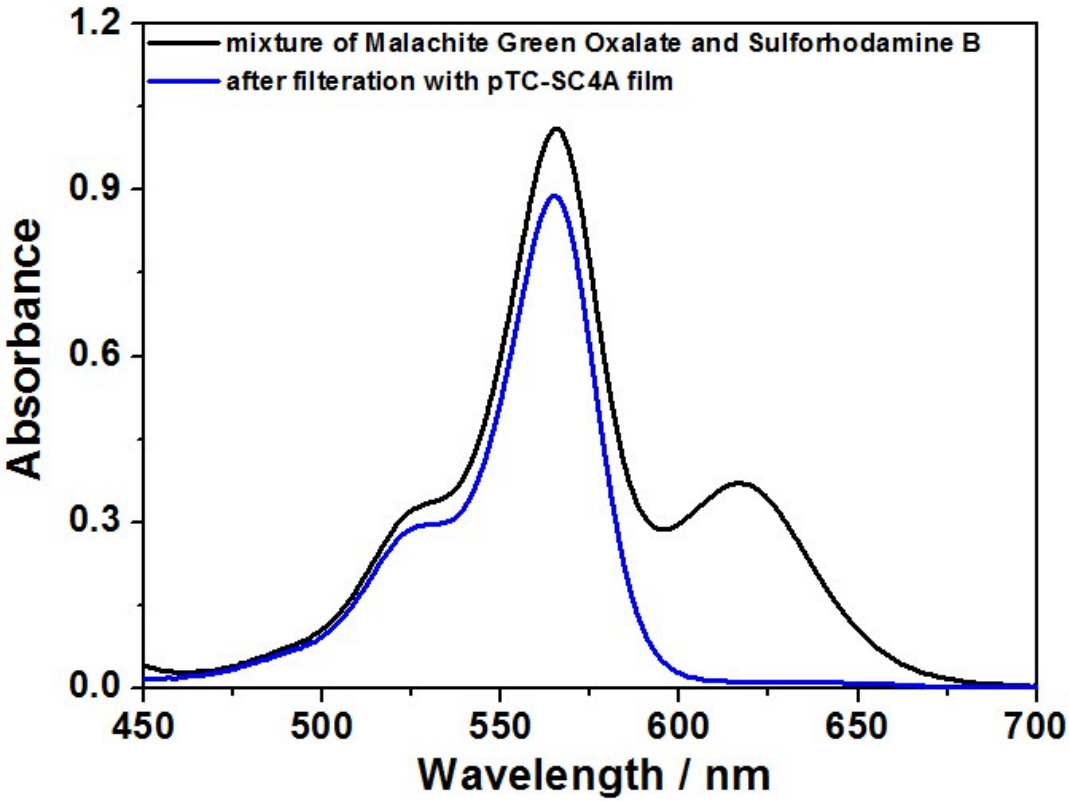

Figure S27. **UV-Vis spectra of malachite green oxalate (MGO) and sulforhodamine B (sRhB) mixture before (black) and after (blue) filtration with pTC-SC4A film.** Two kinds of dyes (MGO and sRhB) with opposite charge can be effectively separated by pTC-SC4A membrane. The sRhB passed through the film very well with the loss less than 5%, and the MGO was totally removed.

Reference

1. (a) Ogoshi, T.; Kanai, S.; Fujinami, S.; Yamagishi, T.-a.; Nakamoto, Y. *J. Am. Chem. Soc.* **2008,** *130*, 5022; (b) Fernández-Abad, S.; Pessêgo, M.; Basílio, N.; García-Río, L. *Chem. Eur. J.* **2016,** *22*, 6466.

2. Gutsche, C. D.; Bauer, L. J. *J. Am. Chem. Soc.* **1985,** *107*, 6052.