Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2022

Supporting Information

Long-lived Room Temperature Phosphorescence from Amorphous Non-traditional Intrinsic Clusteroluminescence Polymers

Kang Chen,[a] Yaling Wang,[c] Bo Chu,[d] Zishan Yan,[a] Hairu Li,[c] Haoke Zhang,[d] Shengliang Hu,[c] Yongzhen Yang,[a,b] Bin Liu,*[c] and Xing-Hong Zhang*[d]*

[a] Key Laboratory of Interface Science and Engineering in Advanced Material, Ministry of Education, Taiyuan University of Technology, Taiyuan 030024, P. R. China.

[b] Shanxi-Zheda Institute of Advanced Materials and Chemical Engineering, Taiyuan 030032, China.

[c] School of Energy and Power Engineering, North University of China, Taiyuan 030051, P. R. China.

[d] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China.

Experimental section

Materials

Styrene, maleic anhydride, polyacrylic acid (PAA), toluene and chromatographic grade tetrahydrofuran (THF) were purchased from Shanghai Macklin Biochemical Co., Ltd. Styrene and toluene were purified by atmospheric and vacuum distillation, and maleic anhydride was vacuum sublimated twice to remove maleic acid. Hydrolyzed polymaleic anhydride (HPMA) and azodiisobutyronitrile (AIBN) were obtained from Aladdin Reagent Co., Ltd. AIBN was recrystallized before using, and detailed

purification method for HPMA is given in the “Purification of HPMA” of the Support Information. Anhydrous ethanol, LiOH, NaOH and KOH were obtained from Tianjin Guangfu Technology Development Co., Ltd. Deionized water was used in all the experiments.

Characterization

The samples were characterized by proton nuclear magnetic resonance (^{1}H NMR), gel permeation chromatography (GPC), fluorescence-phosphorescence spectrophotometer, fourier transform infrared spectroscopy (FT-IR), and UV-vis spectrophotometer. ^{1}H NMR spectra were measured on a Bruker Avance DMX 400 MHz instrument using tetramethylsilane as internal reference and DMSO-d_6/D_2O as solvent. The number-average molecular weight (M_n) and polydispersity index (PDI) were characterized with chromatographically pure THF at 40 °C using the PL-GPC 220 chromatograph. FT-IR spectra were taken on a Bruker TENSOR 27 spectrometer. Photoluminescence (PL), time-resolved and phosphorescence lifetime spectra were collected from an FS5 spectrometer with excitation sources of 150 W xenon lamp and microsecond pulsed flash lamp. The fluorescence decay curves were recorded on an Instruments FLS980 transient spectrometer. Absolute quantum yields were obtained by integrating sphere with an excitation wavelength of 360 nm.

Synthesis of PSMA

Styrene (5.00 g), maleic anhydride (4.71 g), AIBN (172.5 mg) and toluene (75 mL) were transferred into a 150 mL three-necked flask and reacted at 70 ℃ for 5 h under N_2 atmosphere. THF was then added to the three-necked flask to dissolve the crude product. The resulting PSMA was purified by three precipitations in excess ethanol followed by vacuum drying at 50 °C to a constant weight.

Synthesis of PSMA-H

PSMA (1.00 g) and THF (10 mL) were transferred into a 20 mL flask and stirred for

30 min. Added 0.1 ml of aqueous solution and stirred for 12 h. Repeated the above steps five times. THF was removed by vacuum drying. Afterwards, added 1 mL aqueous solution and stirred for 12 h. Aqueous solution was removed by rotary evaporation and dried under vacuum at 50 °C to a constant weight.

Synthesis of PSMA-Li, PSMA-Na and PSMA-K

LiOH (220.0 mg) solids and deionized water (5 mL) were transferred into a 10 mL flask and stirred well. The solution of lithium hydroxide was obtained. PSMA-H (1.00 g) and THF (10 mL) were transferred into a 20 mL flask and stirred well. Added lithium hydroxide solution into the flask and precipitation was formed. Dried in vacuum overnight at 50 °C to a constant weight. PSMA-Na and PSMA-K were prepared in the same way as above. The mass of NaOH and KOH were 365.0 mg and 515.0 mg, respectively.

Purify of HPMA

HPMA aqueous solution was put into a 100 Da dialysis bag, and the dialysis bag was placed in excess aqueous solution. Aqueous solution was changed every 6 hours. Repeated the above steps five times. Finally, the aqueous solution was removed by rotary evaporation and dried under vacuum at 50 °C to a constant weight.

Purify of PAA

PAA (2.00 g) and deionized water (15 mL) were transferred into a 20 mL flask and stirred well. The resulting PAA was purified by three precipitations in excess THF followed by vacuum drying at 50 °C to a constant weight.

Computational details

All geometric optimizations were performed using the DFT method at the B3LYP/6-31(d) level using the Gaussian 09 procedure. The polymers were replaced by oligomers

of five repeating units. The distances in the polymers were determined using Gaussian view 6.0.

Results and discussion

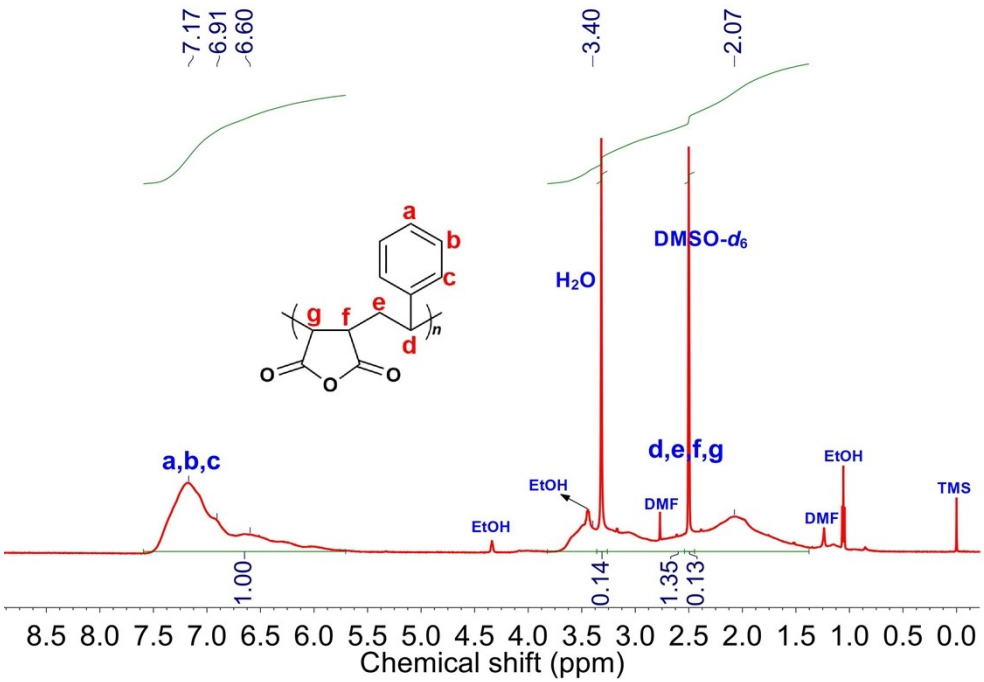


Figure S1. ^{1}H NMR spectrum of PSMA (400 MHz, DMSO-d_6).

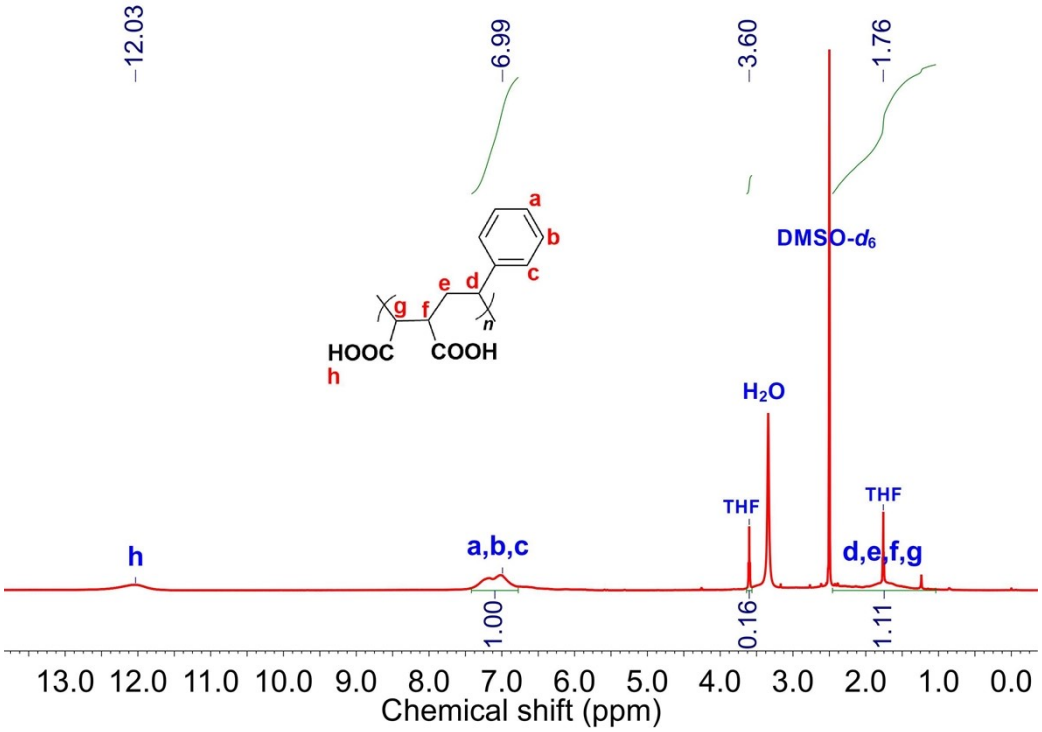


Figure S2. ^{1}H NMR spectrum of PSMA-H (400 MHz, DMSO-d_6).

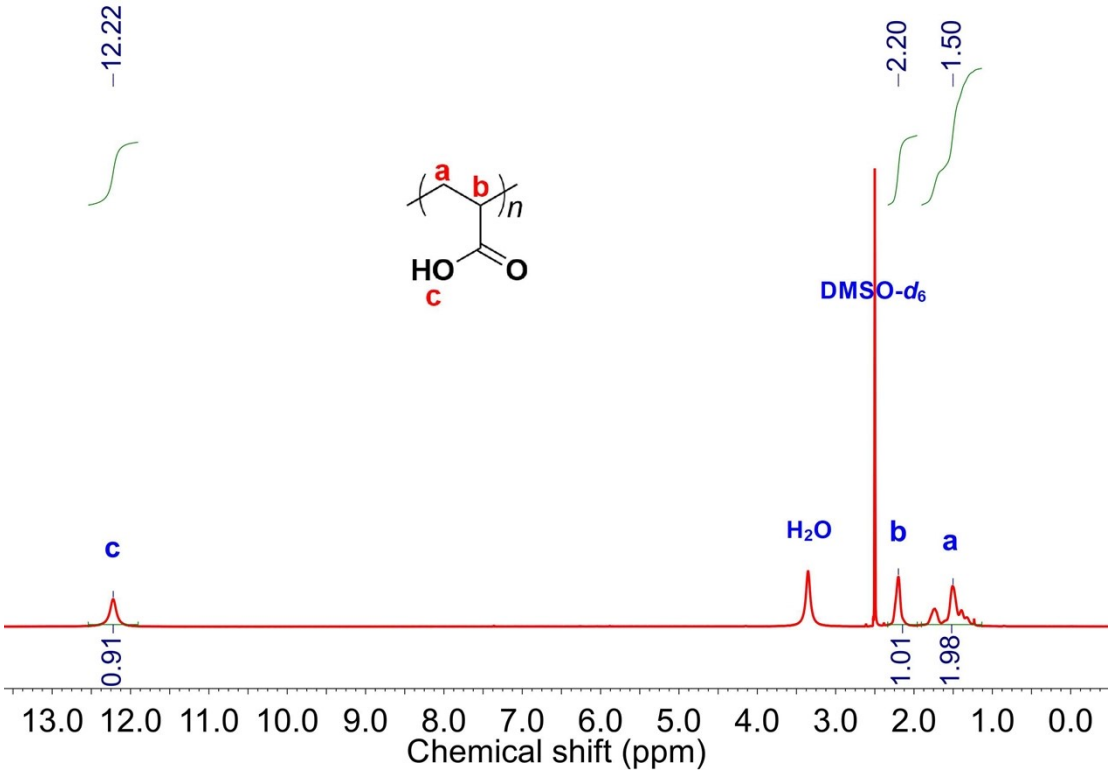


Figure S3. ^{1}H NMR spectrum of PAA (400 MHz, DMSO-d_6).

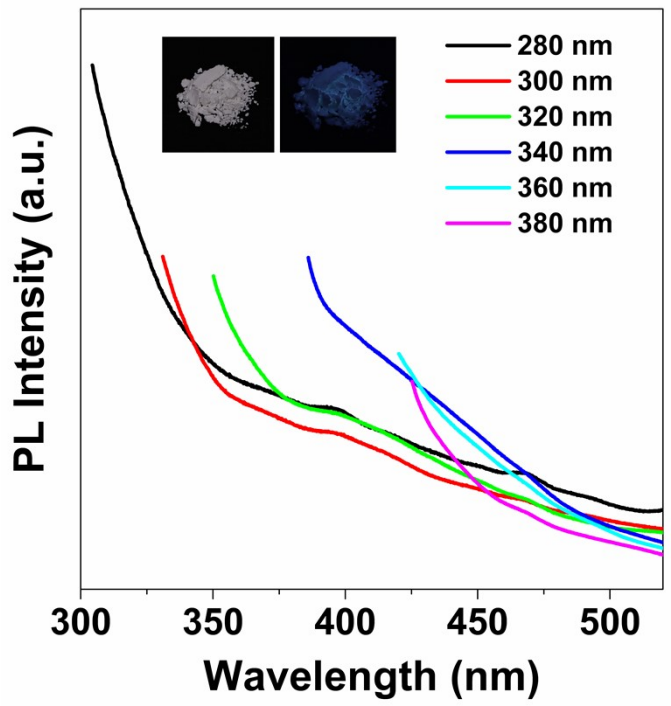


Figure S4. PL spectra of PSMA in solid-state. Inset: photographs of PSMA in daylight (left) and under 365 nm UV light (right).

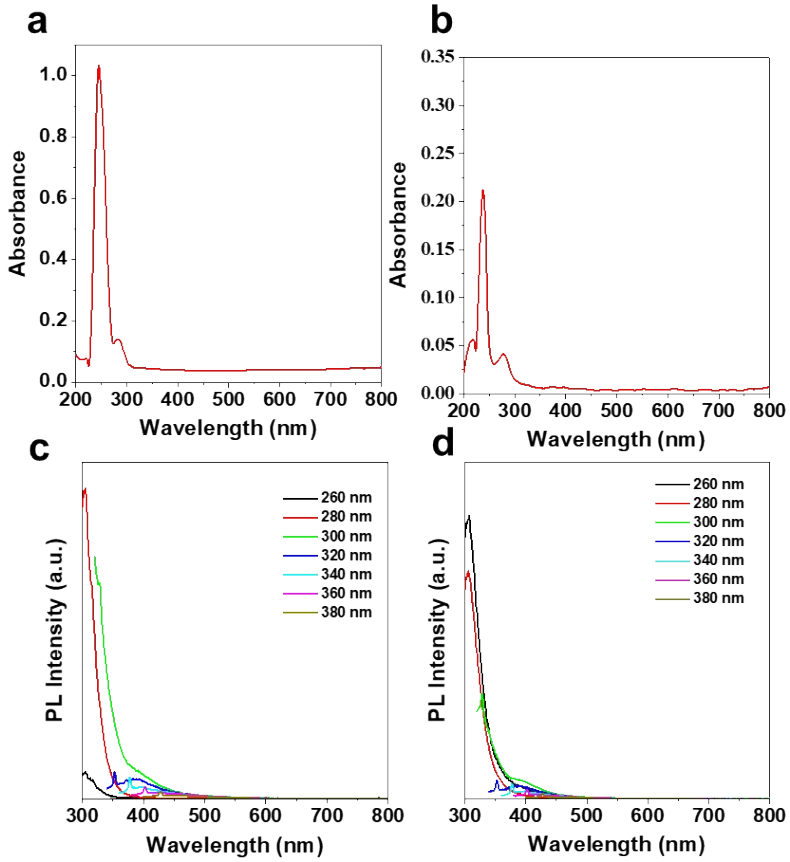


Figure S5. UV-vis absorption spectra of styrene (a) and succinic acid (b) in THF. PL spectra of styrene (c) and succinic acid (d).

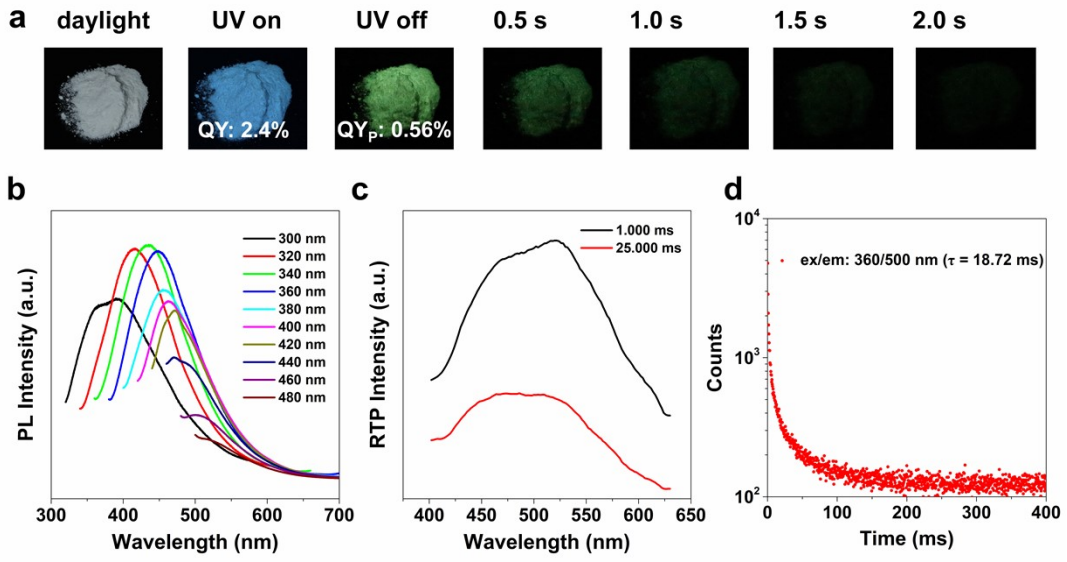


Figure S6. (a) Photographs of solid PSMA-Na taken in daylight, before and after ceasing the 365 nm UV irradiation. (b) PL spectra of PSMA-Na in solid-state under different excitation wavelengths. (c) Time-resolved spectra of PSMA-Na at different delay times in solid-state (phosphorescence mode: λ_{ex}=360 nm). (d) Luminescent delay lifetime of PSMA-K in solid-state at 500 nm (λ_{ex}=360 nm).

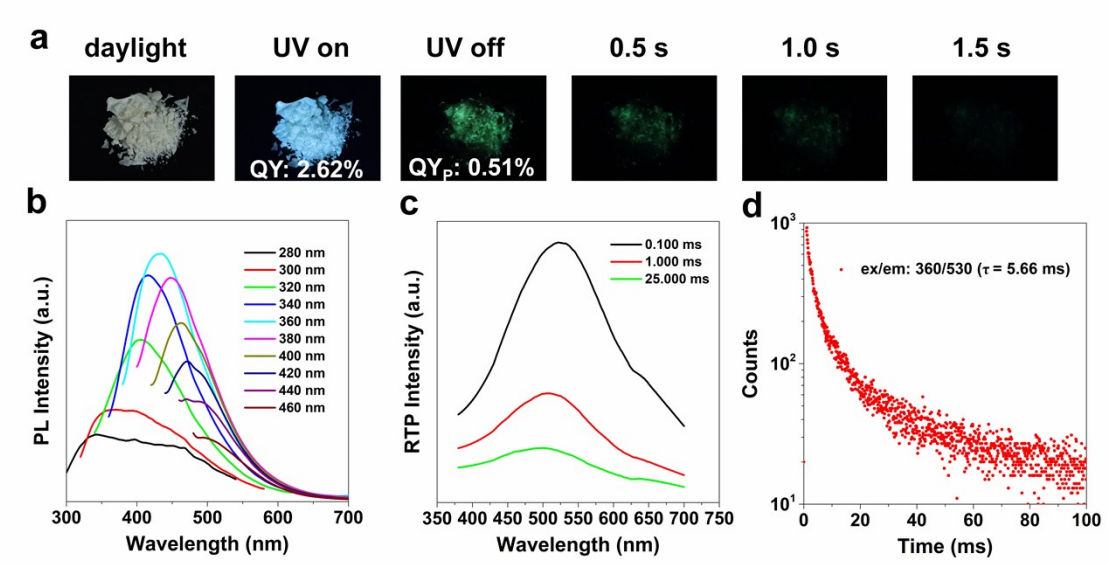


Figure S7. (a) Photographs of solid PSMA-K taken in daylight, before and after ceasing the 365 nm UV irradiation. (b) PL spectra of PSMA-K in solid-state under different excitation wavelengths. (c) Time-resolved spectra of PSMA-K at different delay times in solid-state (phosphorescence mode: λ_{ex}=360 nm). (d) Luminescent delay lifetime of PSMA-K in solid-state at 530 nm (λ_{ex}=360 nm).

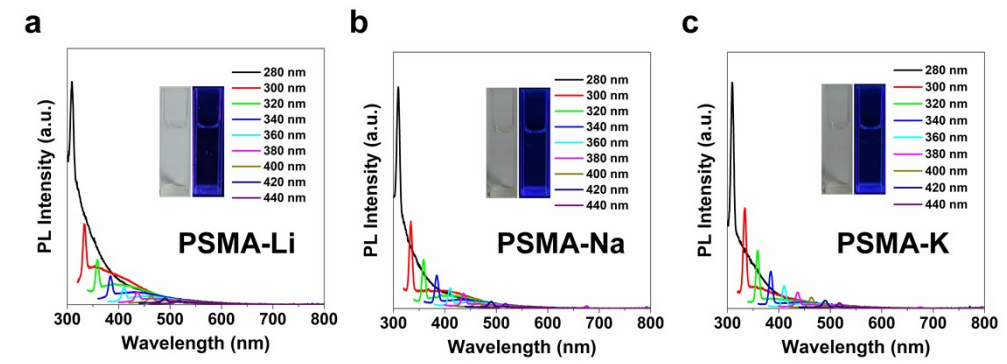


Figure S8. PL spectra of PSMA-R (R=Li, Na, K). Inset: photographs of PSMA-R (R=Li, Na, K,) aqueous solution (10^{-2} M) in daylight (left) and under UV light (right).

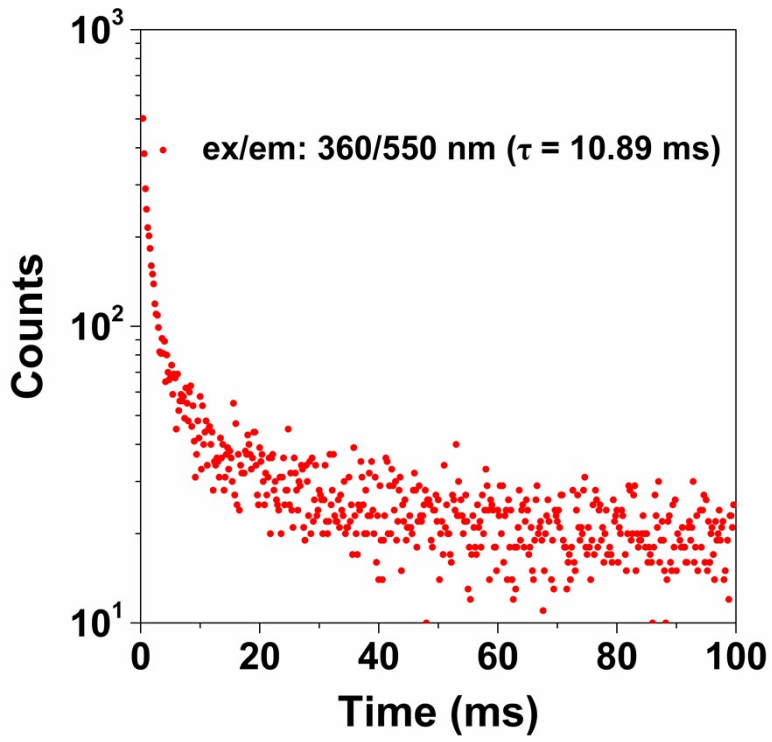


Figure S9. Luminescent delay lifetime of HPMA in solid-state at 550 nm (λ_{ex}=360 nm).

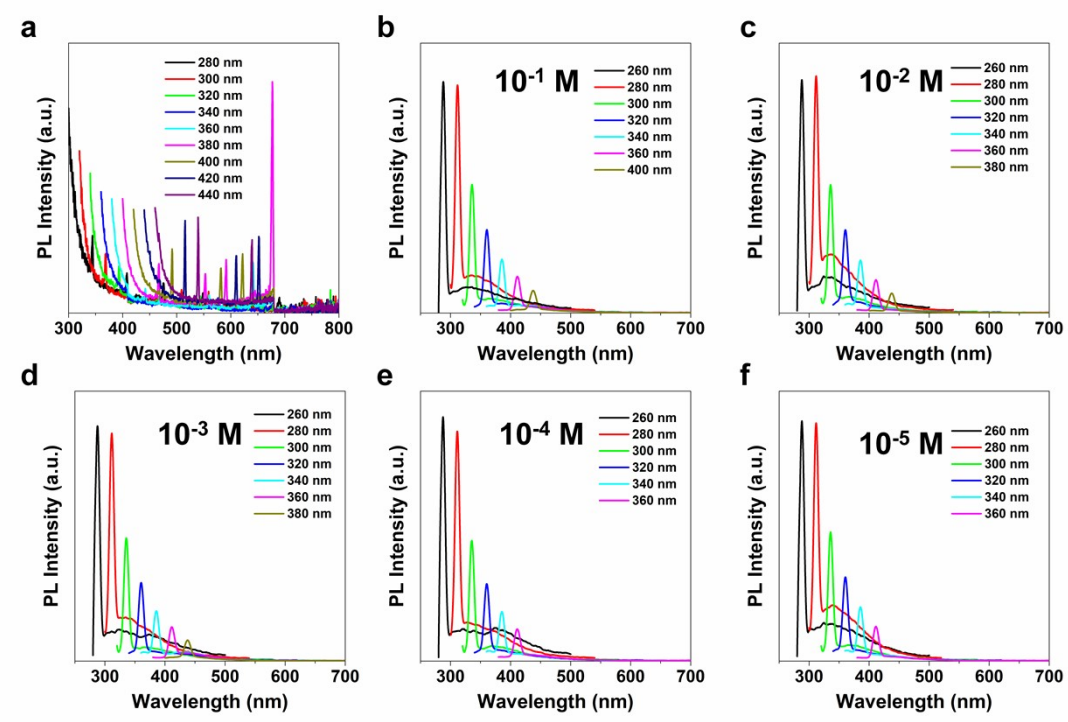
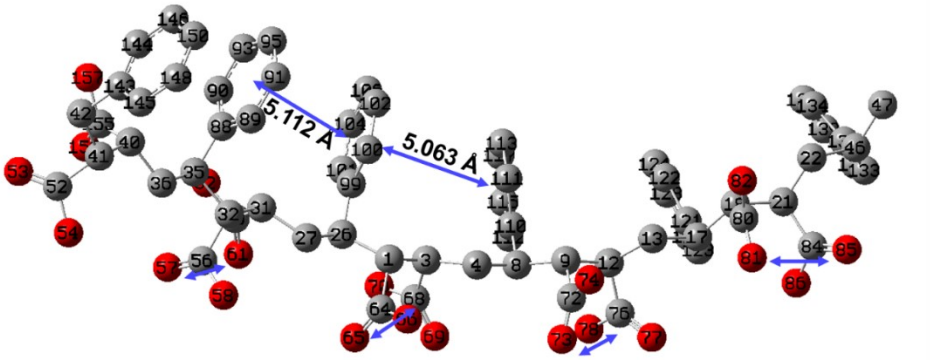


Figure S10. (a) PL spectra of PAA in solid-state and (b-f) PL spectra of PAA aqueous solution at different concentration.

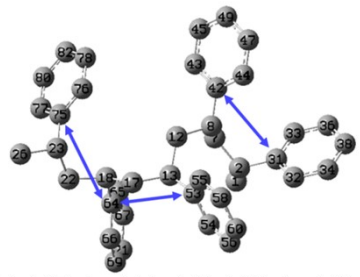
Table S1. Conformational parameters of optimized model of PSMA-H



O57…O61=3.121 Å O65…C68=2.989 Å O73…C76=2.979 Å O81…O85=3.186 Å

O…C	distance (Å)	C…C/O…O	distance (Å)
$O_{53}…C_{155}$	3.146	$C_{88}…C_{143}$	5.235
$O_{52}…C_{156}$	3.191	$C_{88}…C_{99}$	5.113
$O_{61}…C_{16}$	3.275	$C_{99}…C_{110}$	5.056
$O_{57}…C_{60}$	2.967	$C_{110}…C_{121}$	5.071
$O_{65}…C_{68}$	2.989	$C_{121}…C_{132}$	5.040
$O_{69}…C_{64}$	3.264	$O_{53}…O_{156}$	3.302
$O_{73}…C_{76}$	2.979	$O_{57}…O_{61}$	3.121
$O_{77}…C_{72}$	3.281	$O_{65}…O_{69}$	3.216
$O_{81}…C_{84}$	2.970	$O_{73}…O_{77}$	3.213
$O_{85}…C_{80}$	3.322	$O_{81}…O_{85}$	3.186
$O_{53}…C_{143}$	4.362		
$O_{57}…C_{88}$	4.453		
$O_{65}…C_{99}$	4.445		
$O_{73}…C_{110}$	4.447		
$O_{81}…C_{121}$	4.458		

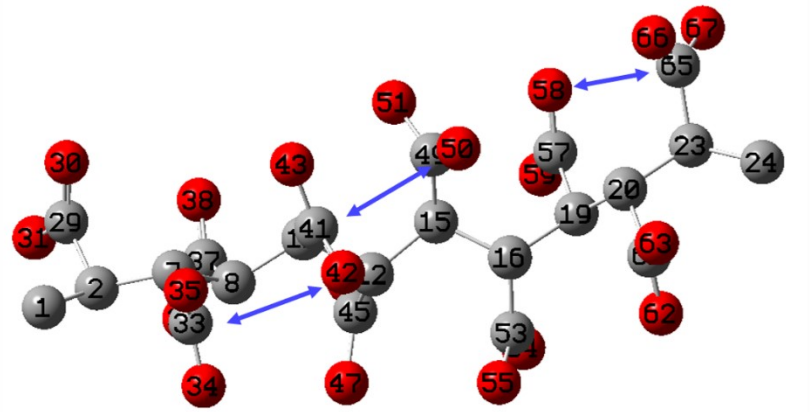
Table S2. Conformational parameters of optimized model of PS



C75…C64=4.379 Å C31…C42=3.956 Å C64…C53=4.332 Å

C…C	distance (Å)	C…C	distance (Å)
$C_{64}…C_{75}$	4.379	$C_{42}…C_{31}$	3.956
$C_{64}…C_{53}$	4.332	$C_{53}…C_{42}$	4.508

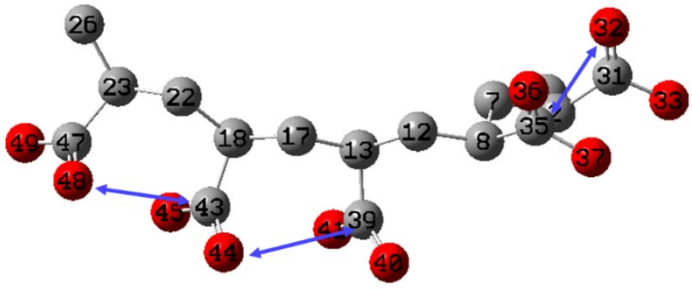
Table S3. Conformational parameters of optimized model of HPMA



O42…C33=3.024 Å O50…C41=3.083 Å O58…C65=2.813 Å

O…C	distance (Å)	O…C	distance (Å)
$O_{30}…C_{37}$	3.627	$O_{34}…C_{41}$	3.645
$O_{38}…C_{29}$	3.022	$O_{42}…C_{33}$	3.024
$O_{38}…C_{45}$	3.605	$O_{42}…C_{49}$	3.543
$O_{46}…C_{37}$	3.047	$O_{50}…C_{41}$	3.083
$O_{46}…C_{53}$	3.687	$O_{50}…C_{57}$	3.640
$O_{54}…C_{45}$	3.254	$O_{58}…C_{49}$	3.051
$O_{54}…C_{61}$	4.280	$O_{58}…C_{65}$	2.813
$O_{62}…C_{53}$	3.171	$O_{66}…C_{57}$	3.922

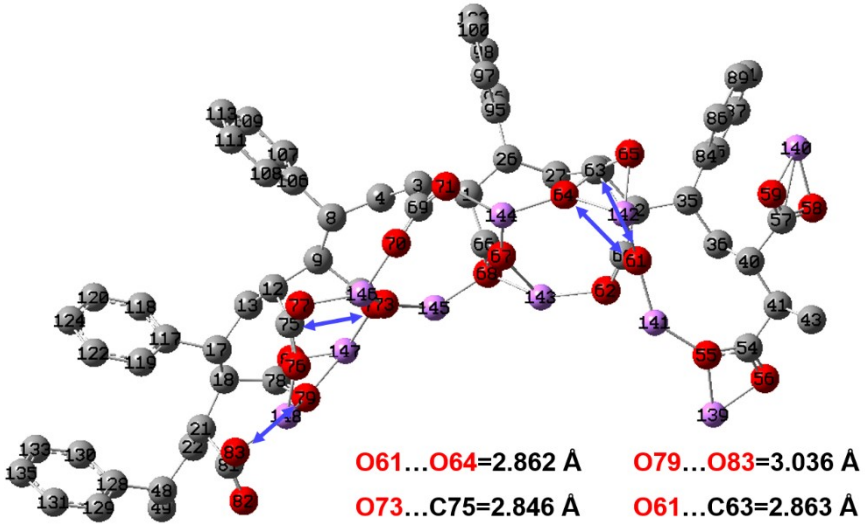
Table S4. Conformational parameters of optimized model of PAA



O48…C43=3.180 Å O44…C39=3.123 Å O32…C35=3.191 Å

O…C	distance (Å)	O…C	distance (Å)
$O_{32}…C_{35}$	3.191	$O_{44}…C_{47}$	3.926
$O_{36}…C_{31}$	3.952	$O_{48}…C_{43}$	3.180
$O_{40}…C_{43}$	3.922	$O_{36}…C_{39}$	5.114
$O_{44}…C_{39}$	3.123	$O_{40}…C_{35}$	4.301

Table S5. Conformational parameters of optimized model of PSMA-Li



O…C	distance (Å)	C…C/O…O	distance (Å)
$O_{79}…C_{81}$	2.940	$C_{128}…C_{117}$	5.097
$O_{83}…C_{78}$	3.433	$C_{117}…C_{106}$	6.020
$O_{76}…C_{72}$	3.128	$C_{106}…C_{95}$	6.138
$O_{73}…C_{75}$	2.846	$C_{95}…C_{84}$	6.182
$O_{67}…C_{69}$	2.851	$O_{79}…O_{83}$	3.036
$O_{71}…C_{66}$	3.334	$O_{73}…O_{76}$	3.103
$O_{61}…C_{63}$	2.863	$O_{67}…O_{71}$	2.984
$O_{64}…C_{60}$	2.978	$O_{61}…O_{64}$	2.862
$O_{83}…C_{128}$	4.766		
$O_{79}…C_{117}$	4.475		
$O_{73}…C_{106}$	4.389		
$O_{67}…C_{95}$	4.424		