Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Ultralong Lifetime Room Temperature Phosphorescence and Dual-band Waveguide Behavior of Phosphoramidic Acid Oligomers

Zheng-Fei Liu, Xue Chen and Wei Jun Jin*

College of Chemistry, Beijing Normal University, Beijing 100875, China

E-mail: wjjin@bnu.edu.cn

Table of Contents

1. Experimental Procedures

1.1 Materials

m-Xylylenediamine (XY, 99%), 4,4'-diaminodicyclohexyl methane (ACM, 98%) and isophorondiamine (IPA, 99%) were purchased from J&K Scientific Ltd. (Beijing, China) 1,3-bis(aminomethyl)cyclohexane (BAC, cis- and trans- mixture, >98%), norbornane dimethylamine (ND, (2,5/2,6-bis(aminomethyl)bicyclo[2.2.1]heptane, a mixture of isomers, >98%) were purchased from TCI Co. (Shanghai, China). Phosphoric acid (>85%), hydrochloric acid (≥36%) and sodium dihydrogen phosphate dihydrate (≥99%) were purchased from Beijing Chemical Reagent Plant. All chemicals were used as received without further purification unless otherwise specified. Dialysis bag was purchased from Spectrum Laboratories Inc. (Los Angeles, United States).

1.2 Synthesis

1.2.1 The preparation of P-XY, P-ND and P-BAC

5.3 mL XY, 6.17g ND or 6.0 mL BAC were dissolved respectively in 20 mL deionized (DI) water in an open round-bottom flask, 5.1 ml concentrated phosphoric acid was dissolved in 20 ml of deionized water, and then the diluted phosphoric acid was slowly dropped into the flask in an ice-water bath under stirring for about half an hour, which was stirred continuously at room temperature for half an hour. The as-formed homogeneous and transparent solution was heated in 80 °C for 1 hours, then the temperature gradually increased to 160 °C at a rate of 20 °C /30 min, and the reaction solution was maintained at 160 °C until the resulting high viscosity liquid product was allowed to solidify upon cooling. Finally the light yellow solid P-XY, P-ND, or colorless solid P-BAC were obtained.

1.2.2 The preparation of PXYONa and PXYOH

18.72 g XY, was dissolved respectively in 10 mL deionized (DI) water in an open round-bottom flask, 10.74 g sodium dihydrogen phosphate dihydrate was dissolved in 20 ml of deionized water, and then the sodium dihydrogen phosphate solution was slowly dropped into the flask in an ice-water bath under stirring for about half an hour, which was stirred continuously at room temperature for half an hour. The as-formed homogeneous and transparent solution was heated in 80 °C for 1 hours, then the temperature gradually increased to 160 °C at a rate of 20 °C /30 min, and the reaction solution was maintained at 160 °C until the water was completely evaporated to obtained white solid, the crude product of PXYONa. A saturated aqueous solution of white solid (pH=9) is poured into a dialysis bag (mwco 100). PXYONa was purified by dialysis against water for 3 days. The 6 M hydrochloric acid was dropped into saturated aqueous solution of white solid, regulating pH to slightly acidic. The acidic solution was poured into a dialysis bag (mwco 100). PXYOH was purified by dialysis against water for 3 days. The reaction process was shown in Figure S1.

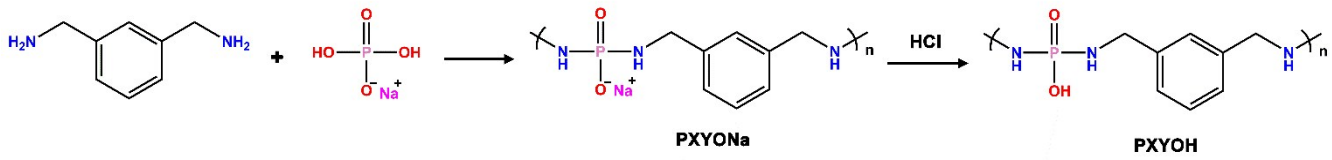


Figure S1. The preparation routes of PXYONa and PXYOH.

1.2.3 The preparation of P-ACM and P-IPA

8.41 g ACM or 6.81g IPA were dissolved respectively in 20 mL deionized (DI) water in an open round-bottom flask, 5.1 ml concentrated phosphoric acid was dissolved in 20 ml of deionized water, and then the diluted phosphoric acid was slowly dropped into the flask in an ice-water bath under stirring for about half an hour, which was stirred continuously at room temperature for half an hour. The as-formed homogeneous and transparent solution was heated in 80 °C for 1 hours, then the temperature gradually increased to 160 °C at a rate of 20 °C /30 min, and the reaction solution was maintained at 160 °C until the resulting high viscosity liquid product was allowed to solidify upon cooling. Finally the oligomers P-ACM or P-IPA were obtained.

1.2.4 The preparation of amorphous P-ND

A 400 μL saturated aqueous solution of P-ND was injected into 10 ml acetone. After 10 minutes of sonication, the sample was filtered out and dried at 100 °C for 10 hours.

1.3 Characterizations and calculations

Total luminescence and phosphorescence spectra, decay of phosphorescence and fluorescence, and absolute quantum yield were all recorded or measured on a FLS980 Spectrometer with a xenon arc lamp (Xe900) and a microsecond flash-lamp (uF900). (Edinburgh Instruments Ltd.). The delay time for measuring phosphorescence spectra was set as 0.1ms. The PL lifetimes (τ) of solid state samples were obtained by fitting the decay curve with a multi-exponential decay function of $I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + \cdots + A_i\exp(-t/\tau_i)$, where A_i and T_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles. The absolute quantum yields of the three oligomers at room temperature were estimated by using an integrating sphere (F-M101, Edinburgh) accessory in FLS980 fluorescence spectrometer.

UV absorption spectra of solution samples were collected on a Purkinje TU-1901 UV-Visible spectrophotometer. UV absorption spectra of solid samples were collected on a PerkinElmer Lambda 950 UV-Visible spectrophotometer.

The PXRD data of P-XY, P-ND, P-BAC were collected at 298 K with a Shimadzu XRD-700 diffractometer with Cu−Kα radiation (X-ray sources, λ = 1.5418Å). Measurement range is set to 5° < 2θ < 80° with the step size of 0.0330°/2ϑ.

FTIR spectra were recorded on a Shimadzu IRAffinity-1 spectrophotometer.

The MS data of P-XY was collected by Bruker autoflex speed LRF MALDI-TOF mass spectrometer with anthratriol as the matrix and aqueous methanol solution as solvent. The MS data of P-BAC and P-ND were collected by SCIEX Triple TOF™ 5600 mass spectrometer in positive-ion mode (electrospray ionization mass spectrometry, ESI-MS) with aqueous methanol solution as solvent.

Aqueous gel permeation chromatography (GPC) experiments were performed on Shimadzu Rid-20A chromatographic instrument. Samples used 0.1 mol/L $NaNO_3$ aqueous solution as mobile phase at 0.6 mL min^{-1} flow rate. Polyethylene glycol was used as the calibration standard.

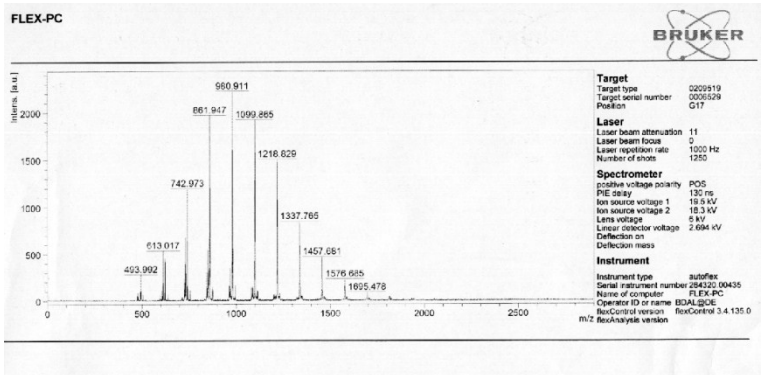
Thermogravimetric analysis experiments were carried out on a PerkinElmer Diamond SII thermal analyzer under nitrogen atmosphere with a heating rate of 5 °C/min from 30 °C to 800 °C. Differntial scanning calorimetry thermograms experiments were measured on a METTLER TOLEDO DSC 1 calorimeter under 50 mL/min nitrogen with a heating rate of 5 ℃/min from 30℃ to 160℃.

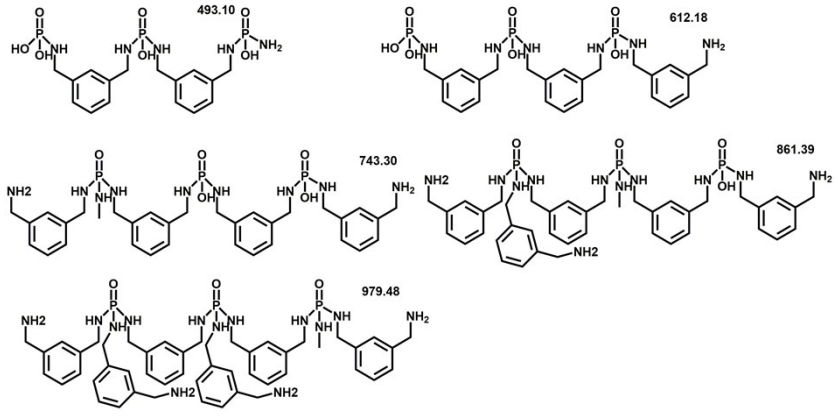
^{1}H NMR spectra were obtained using a JEOL-400 spectrometer.

All calculations were carried out with the GAUSSIAN09 [1] quantum chemistry package. Molecular surface electrostatic potentials (SEP), molecular orbitals and the distribution of Millikan charge were calculated by the TD-B3LYP/6-31G* method. The structures were optimized by the same conditions.

2. Mass spectroscopy

MALDI-TOF mass spectroscopy (MS) of P-XY is shown in **Fig S2**. For P-ND and P-BAC, the attempts to use MALDI-TOF MS are not successful. Therefore, it has to use ESI-MS and the results are shown in **Fig S3-S4**. Due to the difference of ionization methods, the fragmented information obtained by ESI is more scattered than MALDI. According to the fragmented information, the corresponding fragment structures are speculated.





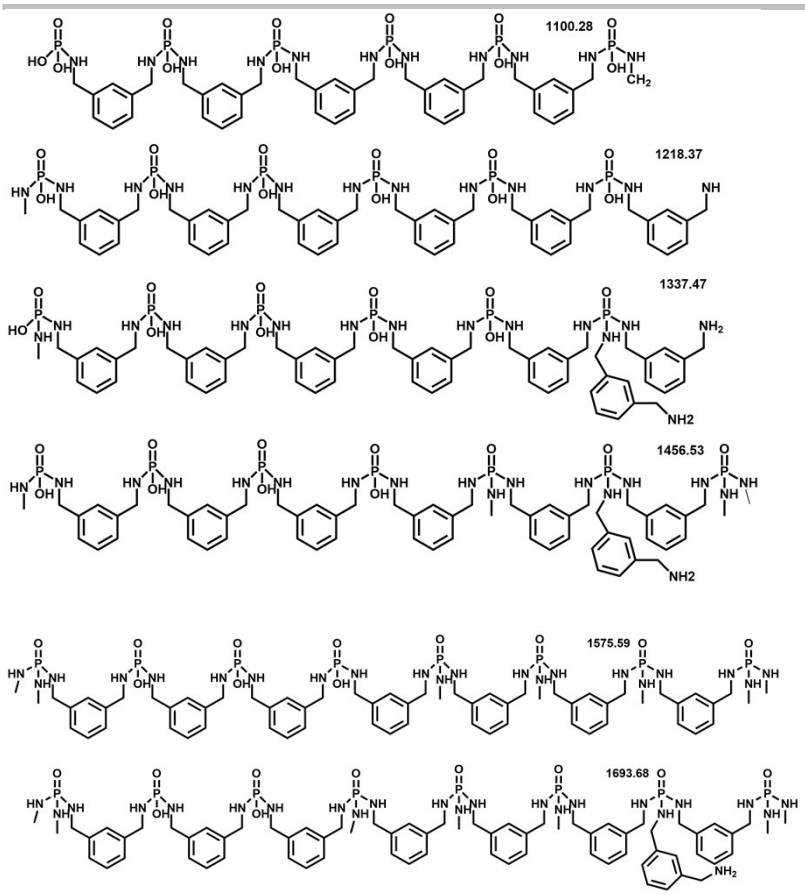
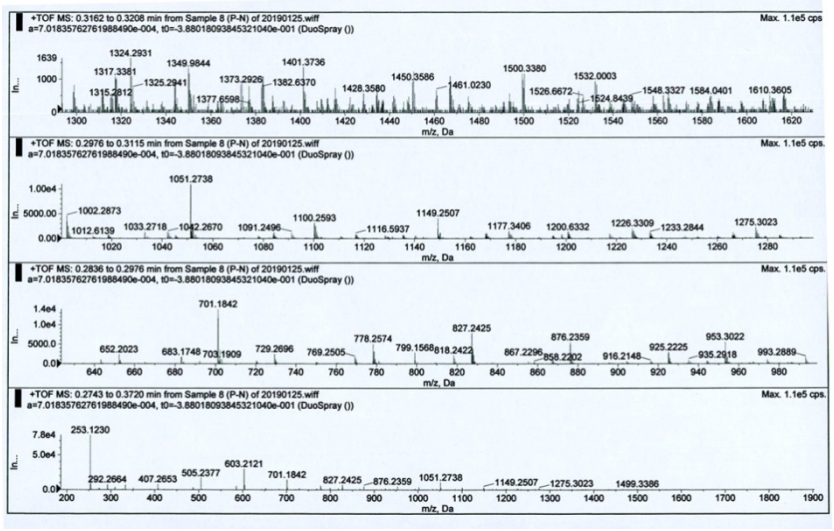


Figure S2.MALDI-TOF MS of P-XY and speculated fragment structures.



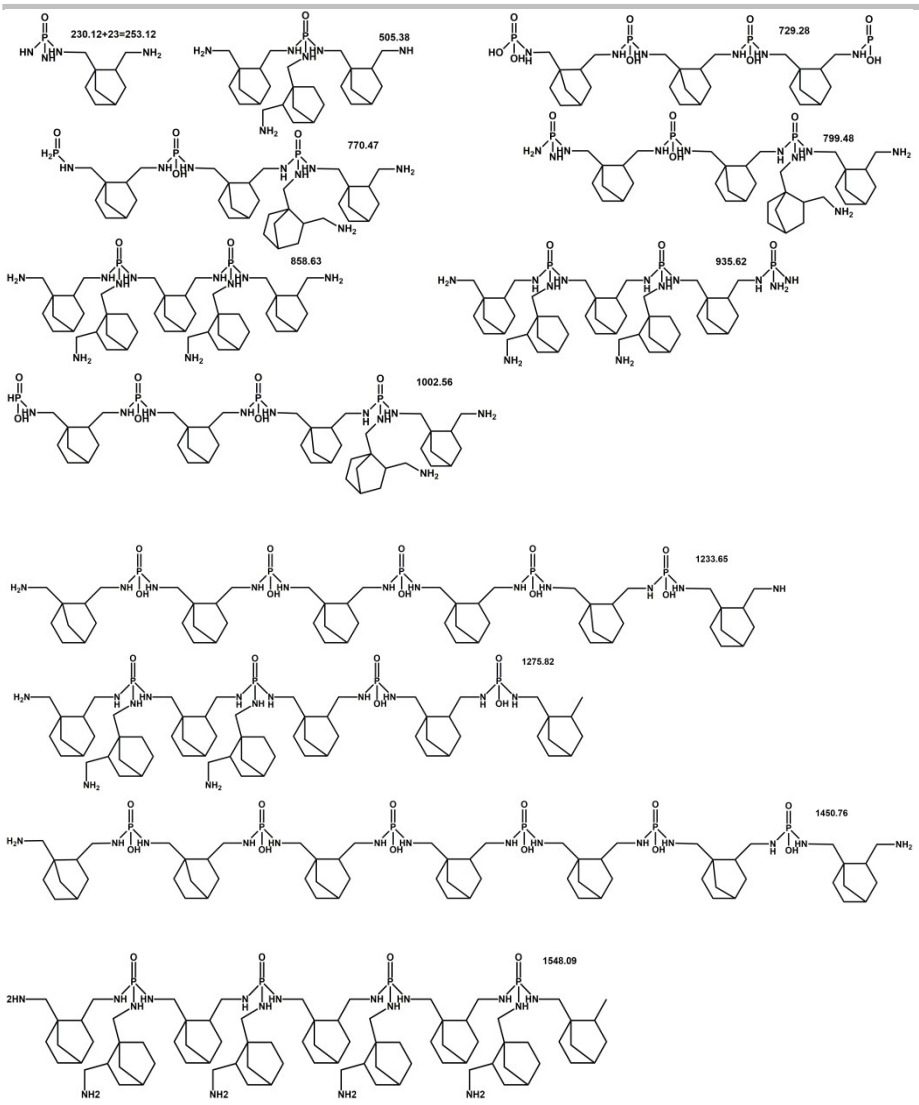
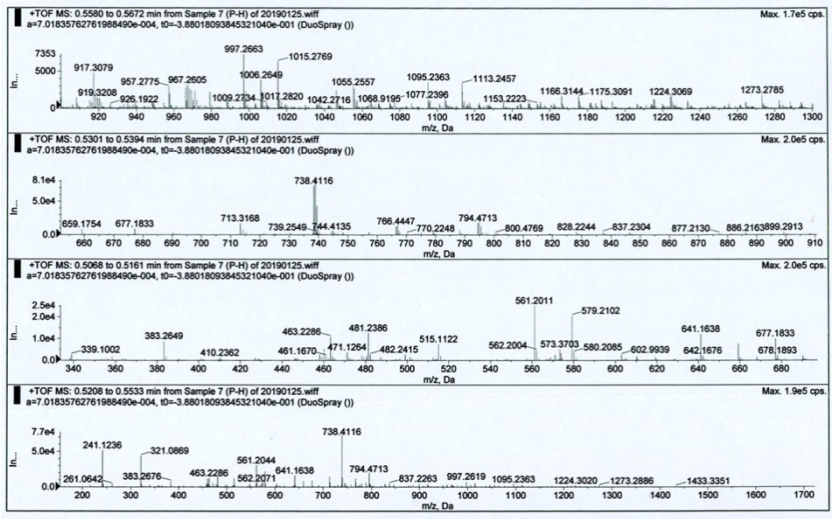


Figure S3. ESI-MS of P-ND and speculated fragment structures.



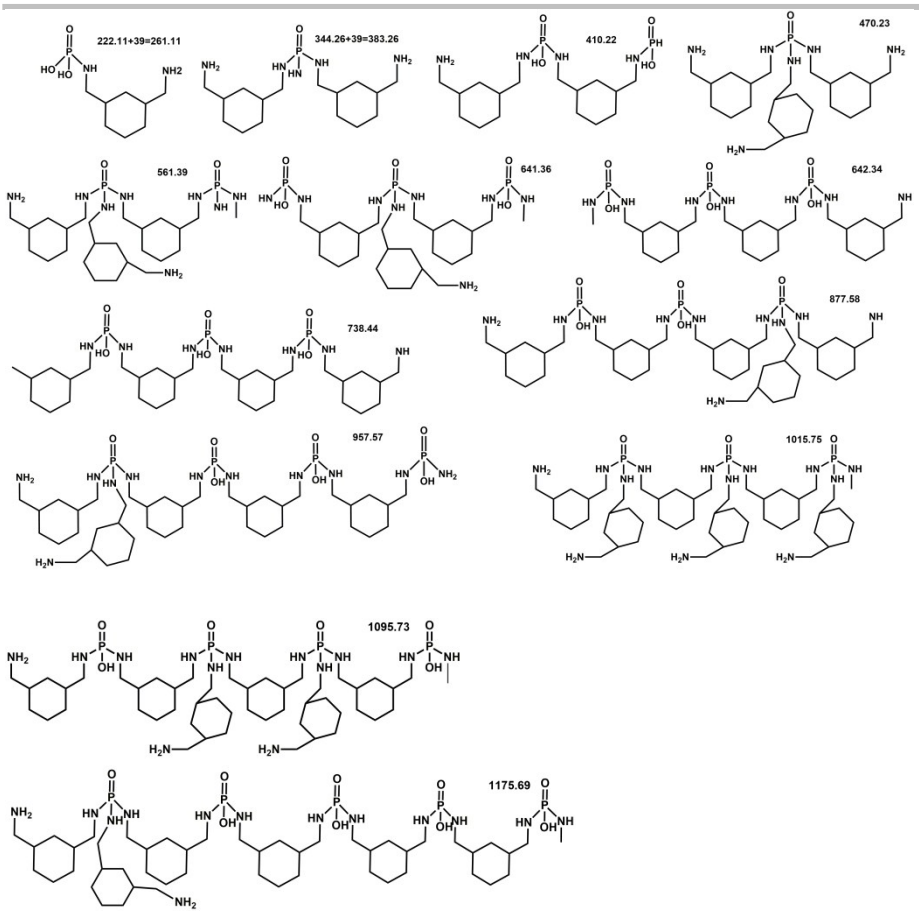


Figure S4. ESI-MS of P-BAC and speculated fragment structures.

3. Gel permeation chromatography

Table S1. The results of gel permeation chromatography.

Samples	P-XY	P-ND	P-BAC
M_n[a]	1089	1156	1146
M_w[a]	1307	1318	1323
PDI[a]	1.2	1.14	1.15

[a] M_n, M_w and PDI mean the number average molecular weight, weight average molecular weight and polymer dispersity index, respectively.

4. Fourier transform infrared spectroscopy of P-XY, P-ND and P-BAC

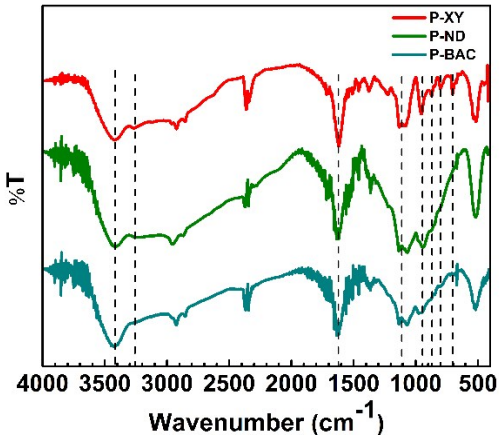


Figure S5. FTIR spectra of P-XY, P-ND and P-BAC solids.

5. PXRD patterns of P-XY, P-ND and P-BAC

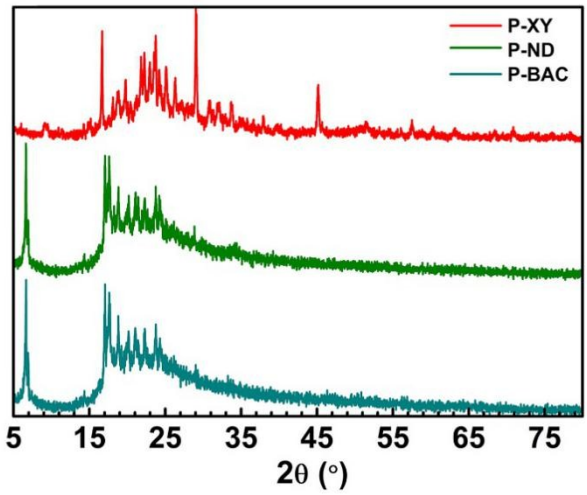


Figure S6. PXRD patterns of P-XY, P-ND and P-BAC solid samples.

6. Thermal stability

The thermal behavior of the three oligomers P-XY, P-ND and P-BAC are studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (**Fig S7**). From the TGA curves, the starting decomposed temperature of P-XY, P-ND and P-BAC can be obtained, which are 246, 235, and 250 °C, respectively, and the glass-transition temperatures are 60, 65 and 40°C, respectively.

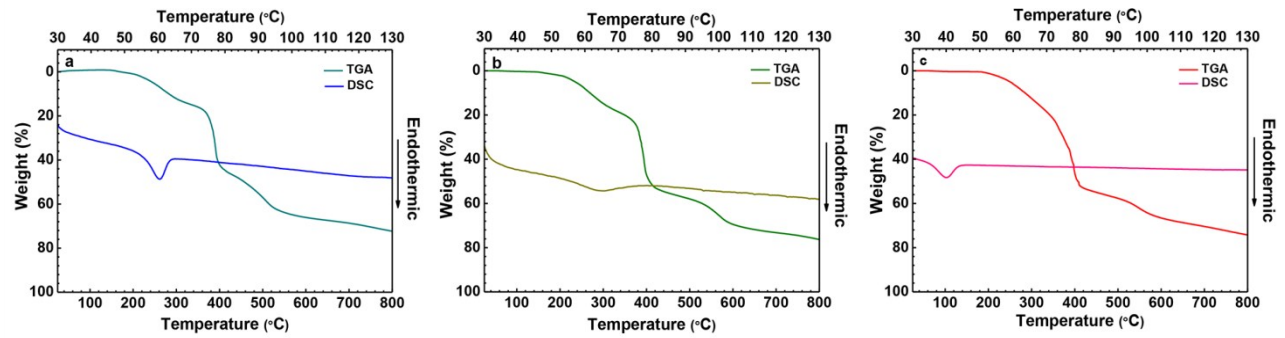


Figure S7. TGA and DSC curves of (a) P-XY, (b) P-ND and (c) P-BAC solid samples.

7. Absorption spectroscopy

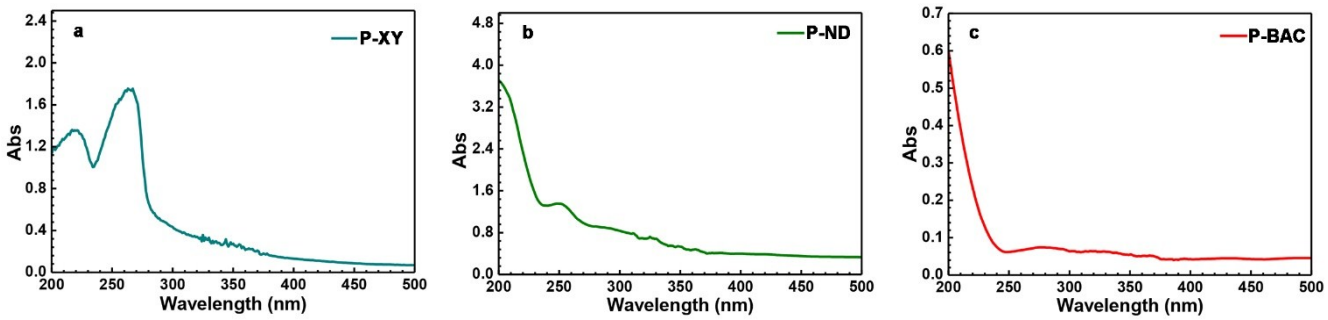


Figure S8. Absorption spectra of (a) P-XY, (b) P-ND and (c) P-BAC in solid.

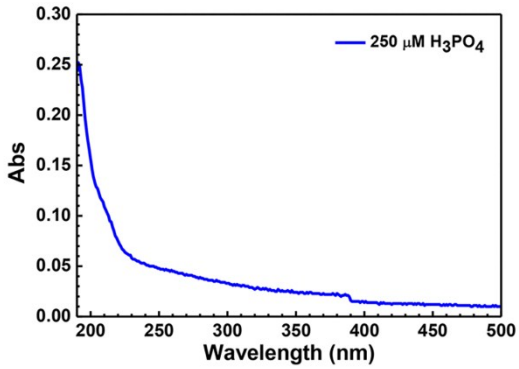


Figure S9. Ultraviolet absorption spectrum of 250 μM phosphoric acid aqueous solution.

As shown in **Fig S8**, all three oligomers display n-π* and π-π* transitions in solid. The π-π* transitions of P-XY, P-ND, and P-BAC are located at 219, 200, and 200 nm, respectively. The n-π* transitions of P-XY, P-ND, and P-BAC are located at 263, 250, and 277 nm, respectively. Generally, the directions of π and π* orbitals of organic molecules are parallel while the n-orbitals are directed at right angles to the π* orbitals, which results in poorer orbital overlap between the n and π* orbitals than between the π and π* orbitals and makes for lower transition efficiency in n-π* transitions. But the absorption of P-XY did not follow the above rule. It is speculated that the n-π* transitions of P-XY is not only localized at P=O in solid. As the distance between chains decreases in solid, the n orbitals of oxygen atoms have the opportunity to overlap with the π* orbitals of benzene ring, which promotes the n-π* transitions between chains, and the probability of n-π* transitions increases largely in solid. Since P-ND and P-BAC do not contain additional π-conjugated groups, the n-π* transitions is only localized at P=O, and the relationship between n-π* transitions and the π-π* transitions follows the above rule. The absorption properties are consistent with that dilution phosphoric acid solution, **Fig S9**, strong peak at 191 nm (π-π*), shoulder-peak at about 210 nm and long trailing line from 226 nm to about 300 nm (n-π*). Generally, the

carbonyl group produces three absorption bands, π-π* transition at 150-170 nm, π-π* transition at 180-200 nm, n-π* transition at 270-300 nm.[2] So, the absorption of >C=O and ≡P=O is very similar.

8. Spectroscopic data

Table S2. Photophysical parameters of solid samples

Samples[a]	λ_{Fl}[b](nm)	λ_{Ph}[b](nm)	τ_{Fl}[c](ns)	τ_{Ph}[b](ms)	Φ_{Total}[c](%)	Φ_{Ph}[d] (%)
P-XY	334/380	317/514	2.40	376.5	35.0	10.5
P-ND	345/396	349/507	2.57	776.9	34.8	8.1
P-BAC	372/419	304/463	4.51	562.9	24.1	4.6

[a] Fl = fluorescence, Ph = phosphorescence. [b] Spectral data is displayed in $\lambda_{ex}/\lambda_{em}$ format. [c] Excitation wavelength is the optimal excitation wavelengths of fluorescence, as shown in **Table S3**. [d] Excitation wavelength is the optimal excitation wavelengths of phosphorescence, as shown in **Table S4**.

9. Excitation and luminescence spectra

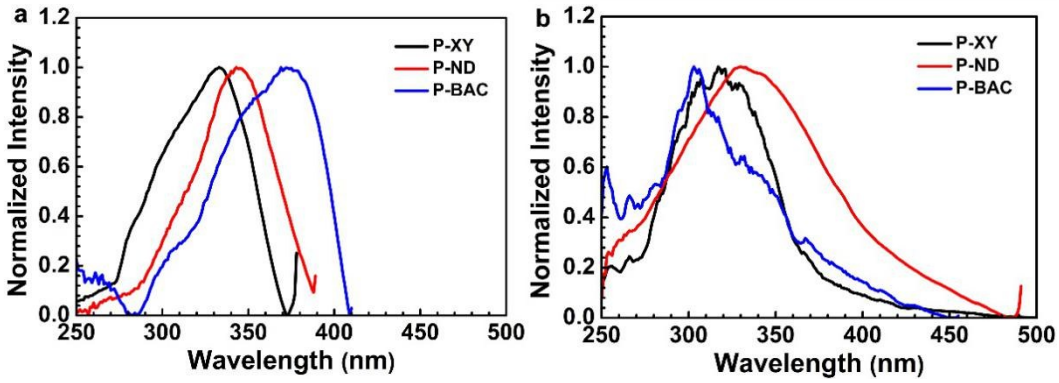


Figure S10. (a) Fluorescence and (b) phosphorescence excitation spectra of P-XY, P-ND and P-BAC solid samples. (Emission wavelength is the optimal emission wavelengths)

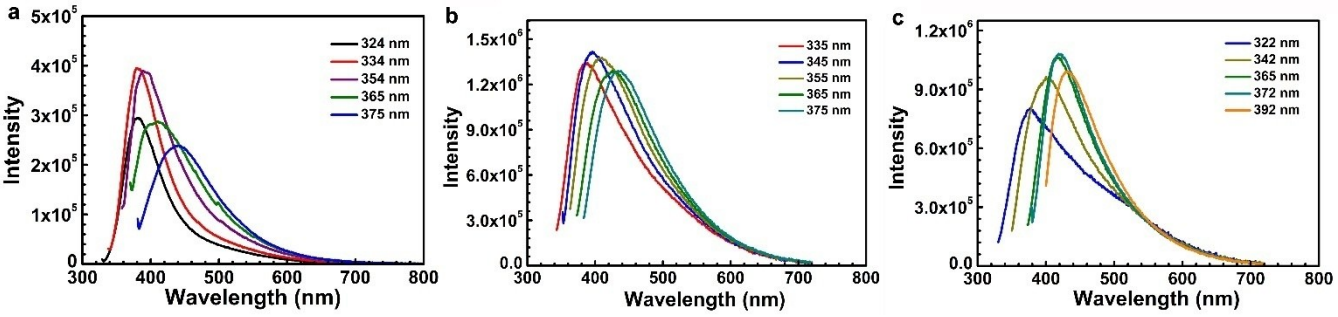


Figure S11. Fluorescence emission spectra with different excitation wavelength of (a) P-XY, (b) P-ND and (c) P-BAC solid samples.

Table S3. Fluorescence spectroscopy parameters of solid samples. (The optimal excitation and emission wavelengths were marked in red)

P-XY		P-ND		P-BAC	
λ_{ex} (nm)	λ_{em} (nm)	λ_{ex} (nm)	λ_{em} (nm)	λ_{ex} (nm)	λ_{em} (nm)
324	381	335	388	322	377
334	380	345	396	342	401
354	389	355	408	365	417
365	408	365	426	372	419
375	441	375	436	392	430

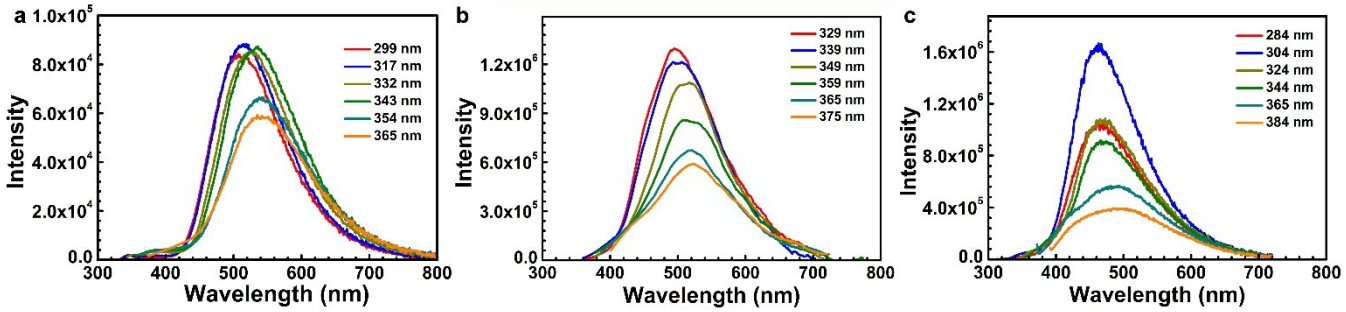


Figure S12. Phosphorescence emission spectra with different excitation wavelength of (a) P-XY, (b) P-ND and (c) P-BAC solid samples.

Table S4. Phosphorescence spectroscopy and decay parameters of samples (the optimal excitation and emission wavelengths were marked in red)

P-XY			P-ND			P-BAC		
λ_{ex} (nm)	λ_{em} (nm)	τ(ms)	λ_{ex} (nm)	λ_{em} (nm)	τ(ms)	λ_{ex} (nm)	λ_{em} (nm)	τ(ms)
299	510	358	329	497	595	284	463	603
317	514	377	339	500	710	304	463	563
332	526	414	349	507	773	324	469	658
343	534	413	359	518	736	344	473	679
354	540	424	365	518	746	365	489	575
365	543	460	375	524	552	384	499	434

10. ^{1}H NMR spectra of PXYONa and PXYOH

The ^{1}H NMR spectra of PXYONa and PXYOH are shown in **Fig S12** and **Fig S13**, respectively, which revealed that methylene protons and phenyl protons of PXYONa and PXYOH. Since PXYONa and PXYOH are only soluble in water, D_2O is selected as the deuterium solvent.

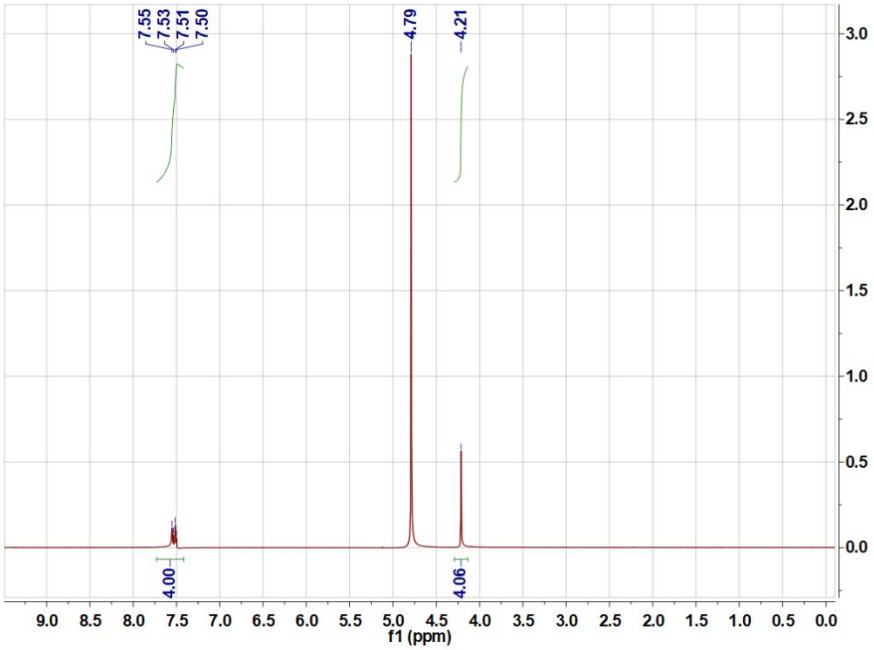


Figure S13.^{1}H NMR spectrum of PXYONa in D_2O.

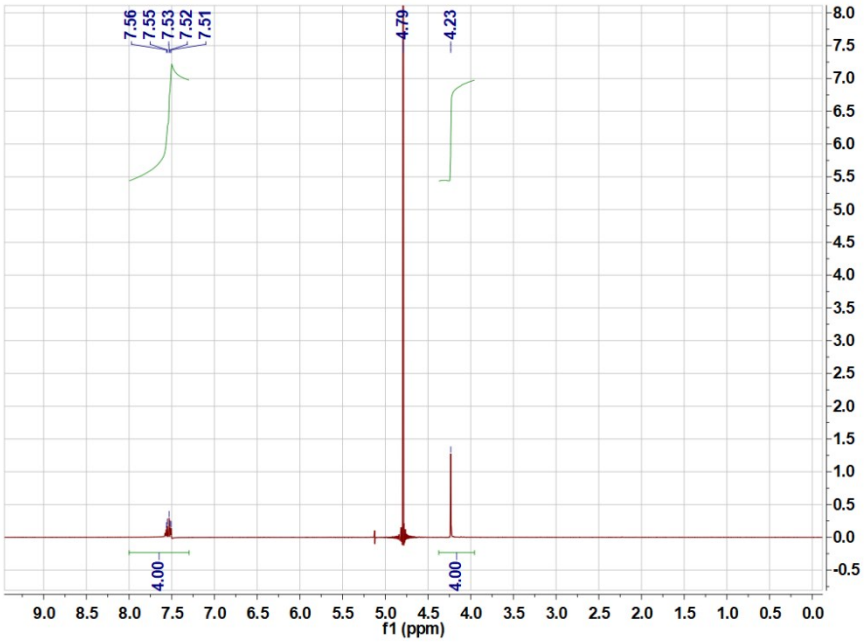


Figure S14.^{1}H NMR spectrum of PXYOH in D_2O.

11. FTIR spectra of PXYONa and PXYOH

The FTIR spectra of PXYONa and PXYOH are shown in **Fig S14**. The change of vibration peak of hydroxyl group (3420 cm^{-1}) proves that sodium salt is acidified into hydroxyl group.

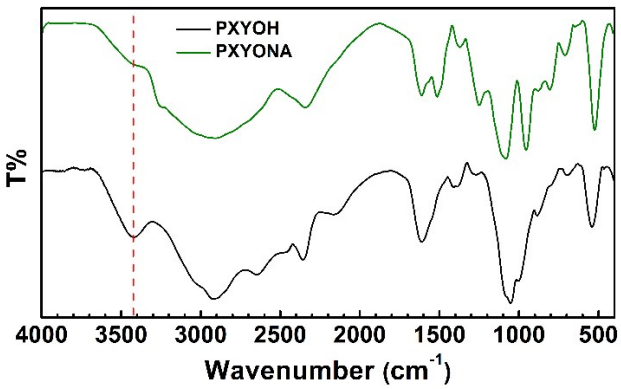


Figure S15. FTIR spectra of solid PXYONa and PXYOH.

12. Excitation and emission spectra of PXYONa and PXYOH

The normalized excitation and emission spectra of PXYONa and PXYOH are shown in **Fig S15**. The change of vibration peak of hydroxyl group (3420 cm^{-1}) proves that sodium salt is acidified into hydroxyl group. No shift in the excitation and emission spectra indicates that the luminophor has not changed.

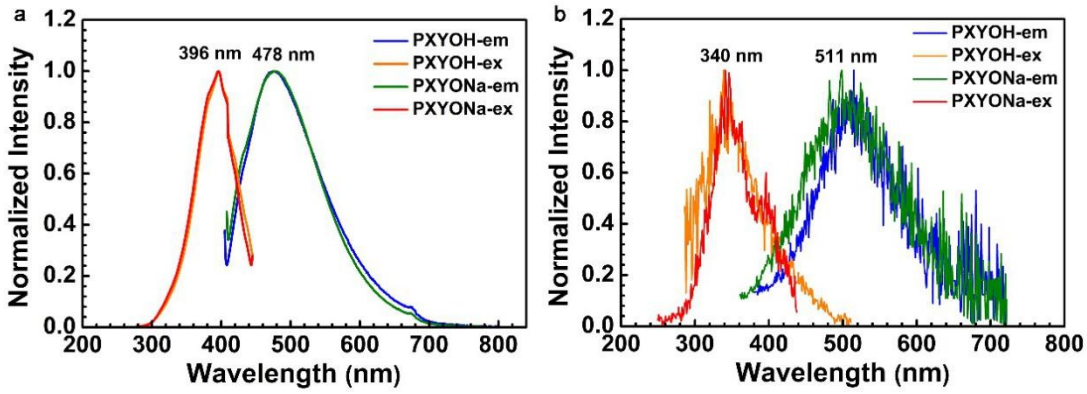


Figure S16. (a) Normalized fluorescence excitation and emission spectra of PXYONa and PXYOH. (b) Normalized phosphorescence excitation and emission spectra of PXYONa and PXYOH.

13. Calculations

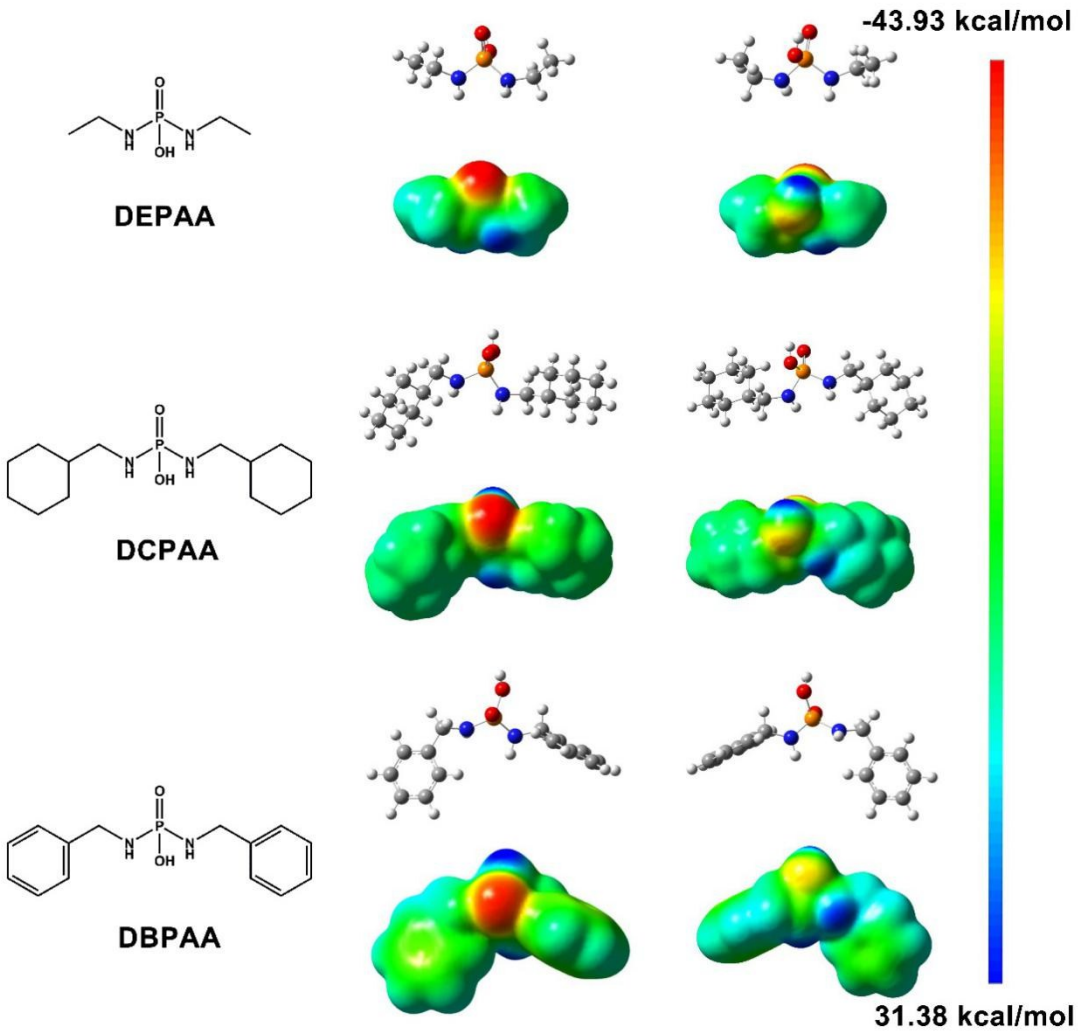


Figure S17. Optimized monomer molecules and their SEP map.

Table S5. Analysis results on SEP map of monomer molecules.

Samples	maximum position	maximum SEP(kcal/mol)	minimum position	minimum potential (kcal/mol)
DEPAA	-N-H	38.34/38.14	-P=O	-51.69
	-O-H	44.96		
DCPAA	-N-H	38.42/37.23	-P=O	-51.10
	-O-H	44.65		
DBPAA	-N-H	38.42/37.23	-P=O	-47.76
	-O-H	47.20		

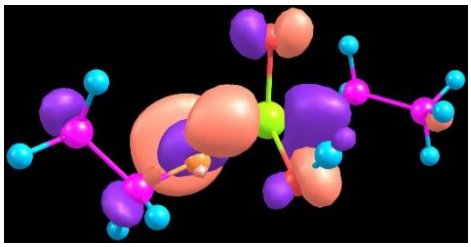


Figure S18.π^* orbital distribution of phosphoryl group in DEPAA molecule.

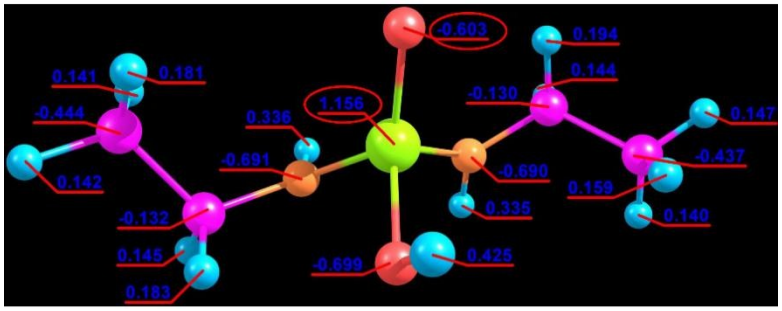


Figure S19. Millikan charge distribution of DEPAA in ground state.

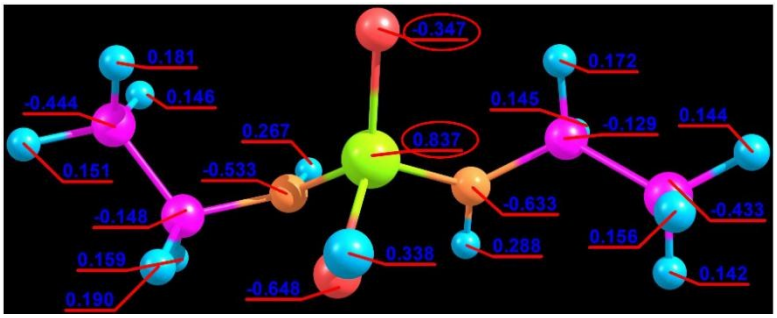


Figure S20. Millikan charge distribution of DEPAA in excited state.

14. Universality confirmation

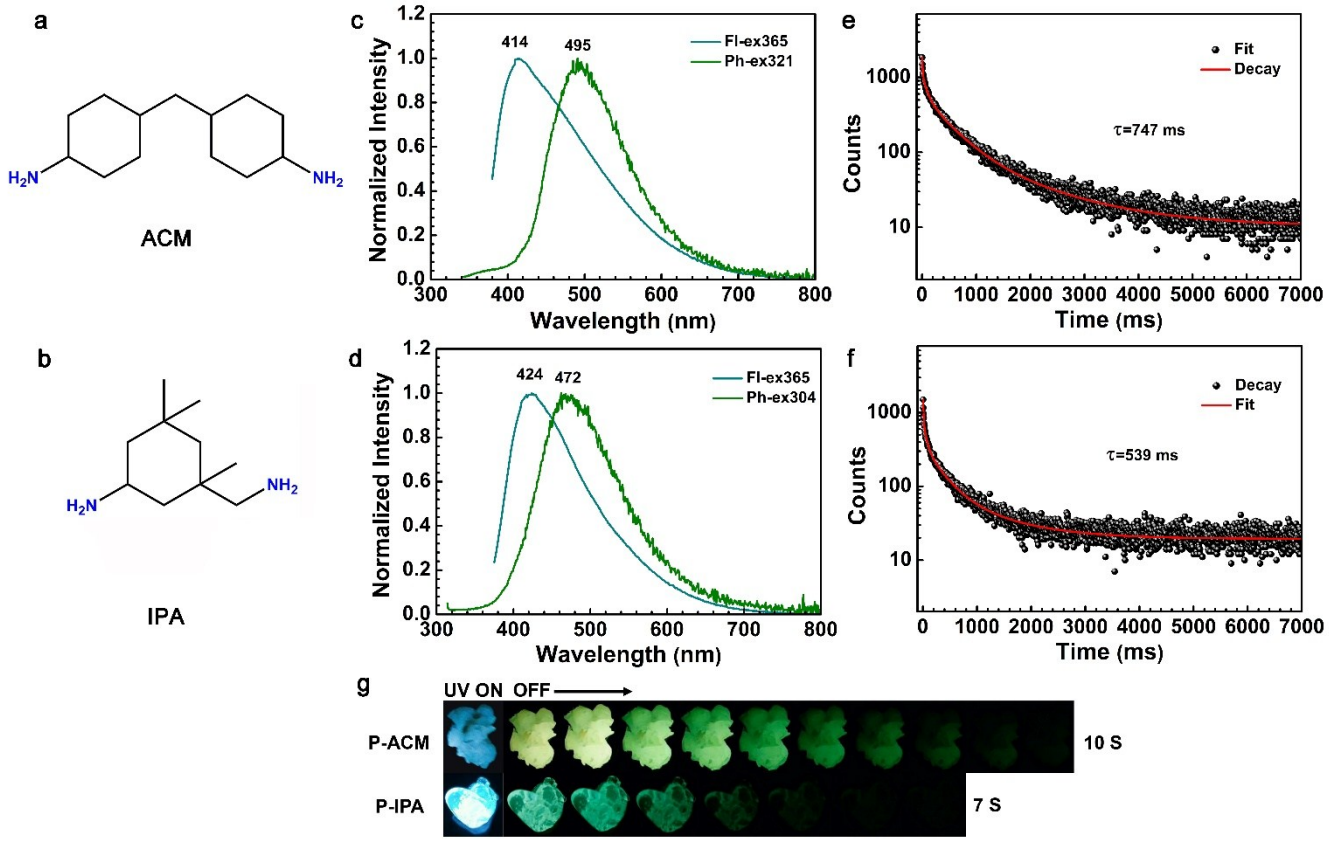


Figure S21. The molecular structures of (a) ACM and (b) IPA. Normalized fluorescence and phosphorescence spectra of (c) P-ACM and (d) P-IPA. Phosphorescence decay profiles of (e) P-ACM and (f) P-IPA. The photographs of P-ACM and P-IPA UV-365 nm radiation and long afterglow after ceasing UV-365 nm radiation in oxygen environment at room temperature (Fl=fluorescence, Ph=phosphorescence).

15. Organophosphoramide vitreous state and easy thermo-processing properties

Three oligomers appear in organophosphoramide vitreous state at the room temperature. When the temperature is slightly higher than their glass transition temperatures, they can be drawn into wires, cast into other any desired shape, which showing good thermo-processing property.

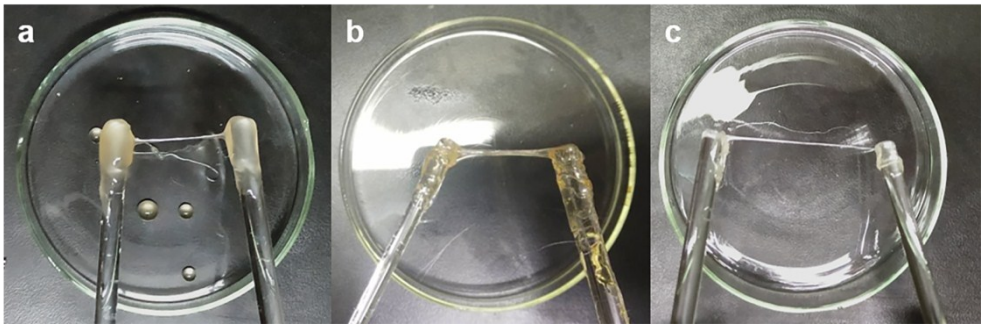


Figure S22. (a) P-XY, (b) P-ND, (c) P-BAC can be drawn into wire at the state slightly higher than glass-transition temperatures.

16. Measurement ofphosphorescence quantum yield

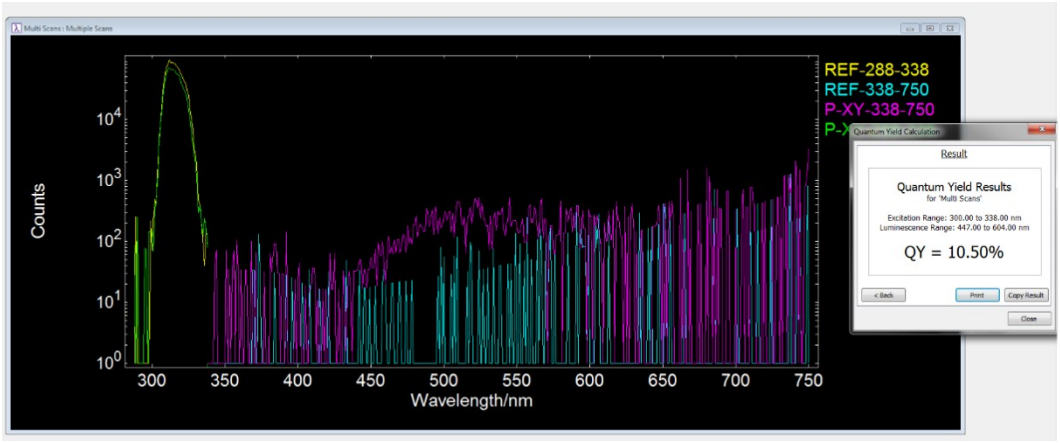


Figure S23. The spectra for measuring phosphorescence quantum yield of P-XY.

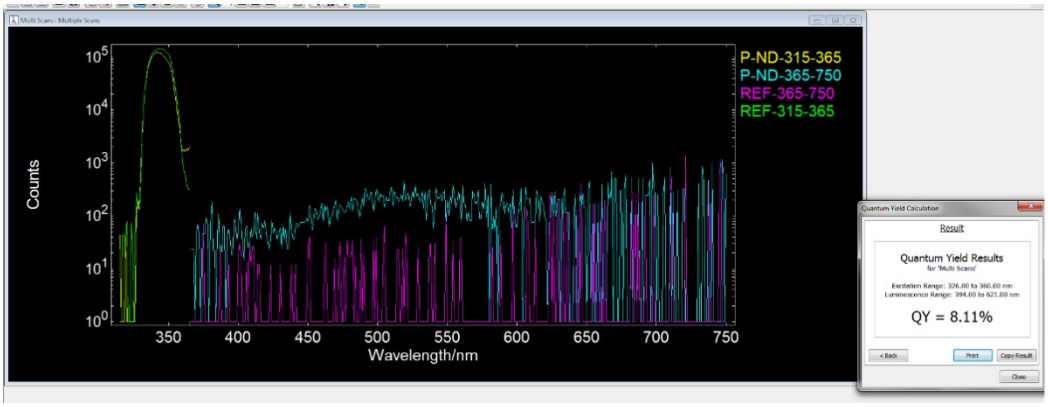


Figure S24. The spectra for measuring phosphorescence quantum yield of P-ND.

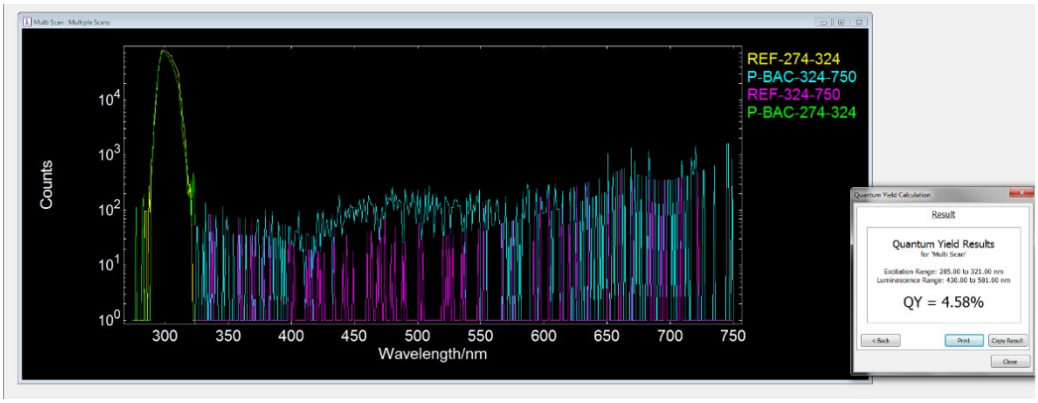


Figure S25. The spectra for measuring phosphorescence quantum yield of P-BAC.

17. Measurement model of optical waveguide

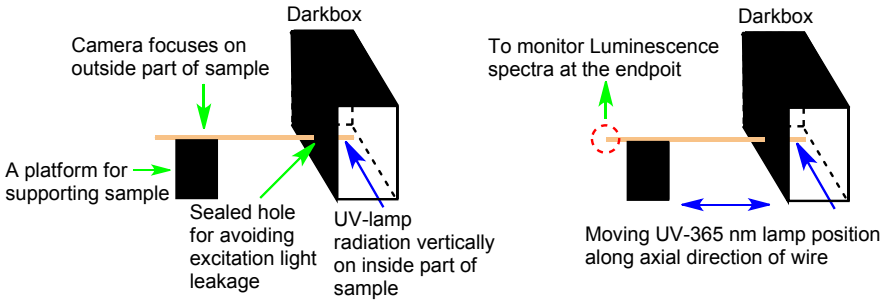


Figure S26. Schematic diagram of experimental equipment for optical waveguide measurement. (left) A UV-365 lamp radiated vertically on the inside part of sample in a dark box. The camera focuses on outside part of sample. Also the hole through which the sample was threaded into the dark box is sealed for avoiding excitation light leakage. (right) Spatially resolved total luminescence spectra of the oligomer wires were scanned at the endpoint by changing excitation light position. All experiments were carried out in dark environment.

References

1. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Gaussian Inc., Wallingford, CT, 2009.
2. E. S. Stern, C. J. Timmons in *Electronic Absorption Spectroscopy in Organic Chemistry*, *3rd*, Edwad Arnold Ltd, London, 1970, pp. 52-53.