Supporting Information

Radical photopolymerization using 1,4-dihydropyrrolo[3,2-b]pyrrole derivative prepared via one-pot synthesis

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Electron paramagnetic resonance (EPR) experiments spectrometer parameters The ESR-ST experiments were carried out using an X-band spectrometer (Bruker EMXPlus). LED lamp of405 nm was used as irradiation source for triggering the production of radicals at room temperature (RT) under N_2-saturated tert-butylbenzene and trapped by phenyl-N-tert-butylnitrone (PBN) according to a procedure described elsewhere in detail.17 The ESR spectra simulations were carried out with the PEST WINSIM program. The sweep width was 200.00G, sweep time was 60.00s, time constant was 0.01ms, modulation frequency was 100.00 kHz, modulation amplitude was 1.00G, microwave powder was 6.325 mW, and the number of X-scans was 1.

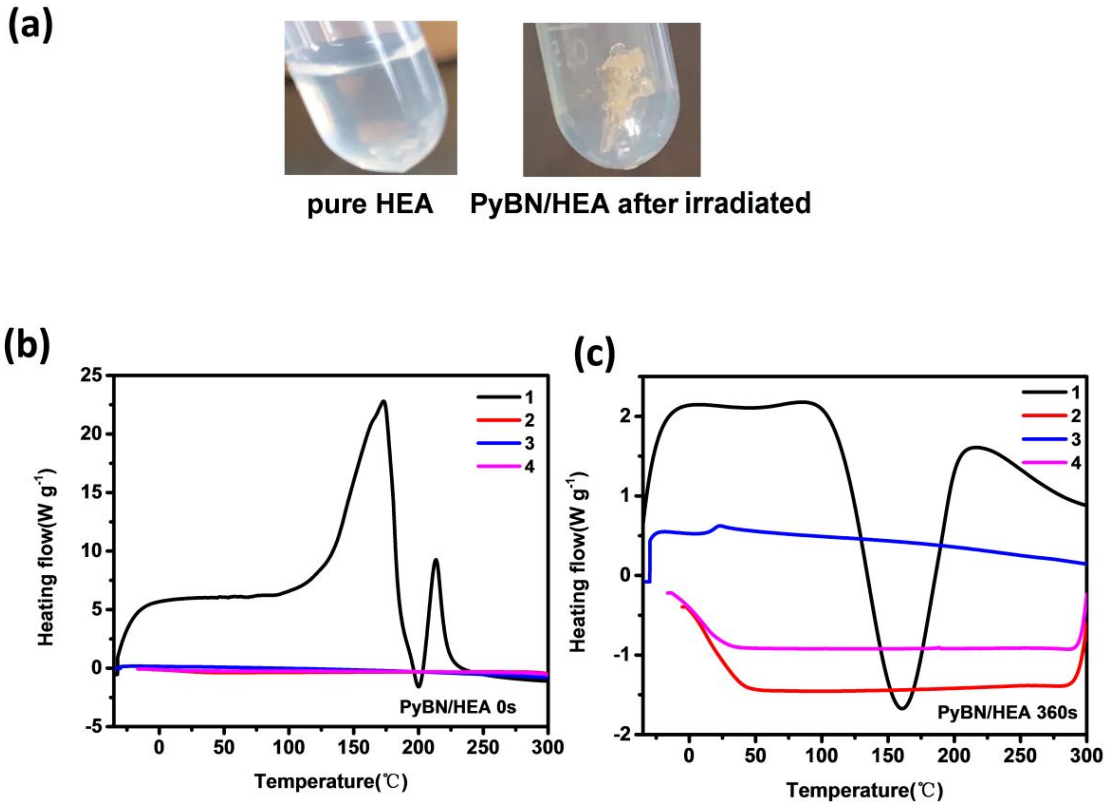


Figure S1. (a) The photos of pure HEA and the product of PyBN/HEA after cured for 360 s. DSC thermograms of PyBN/HEA (b) at 0s and (c) after irradiation of 365-nm LED for 360s.

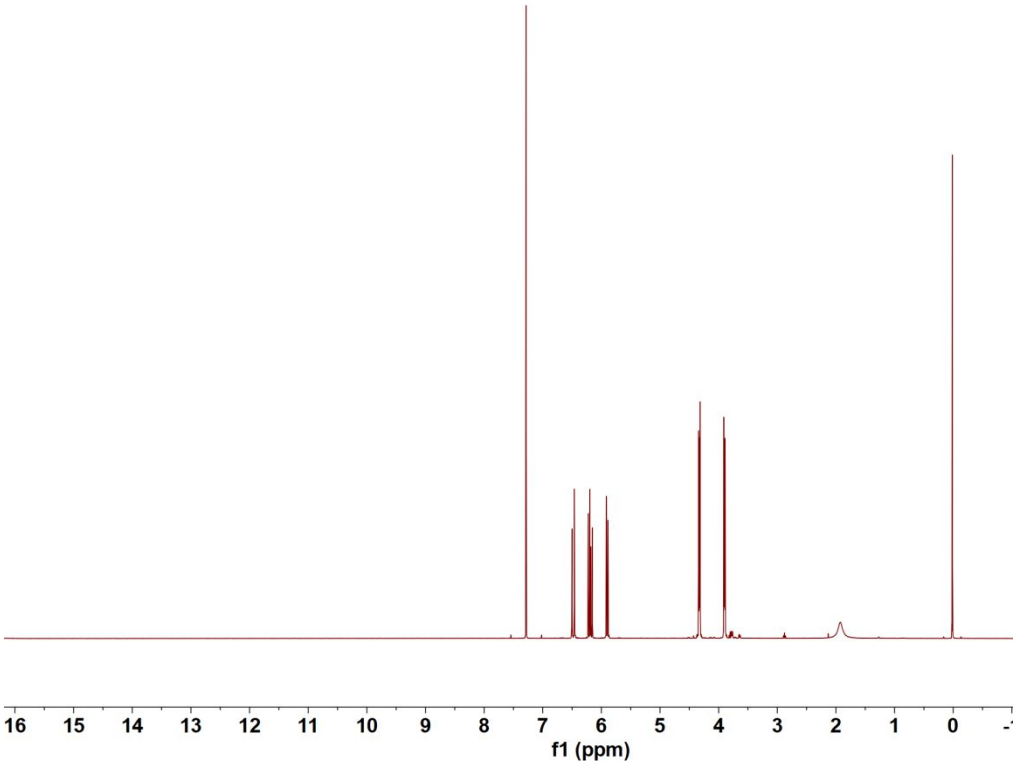


Figure S2. ^{1}H NMR of pure HEA in $CDCl_3$.

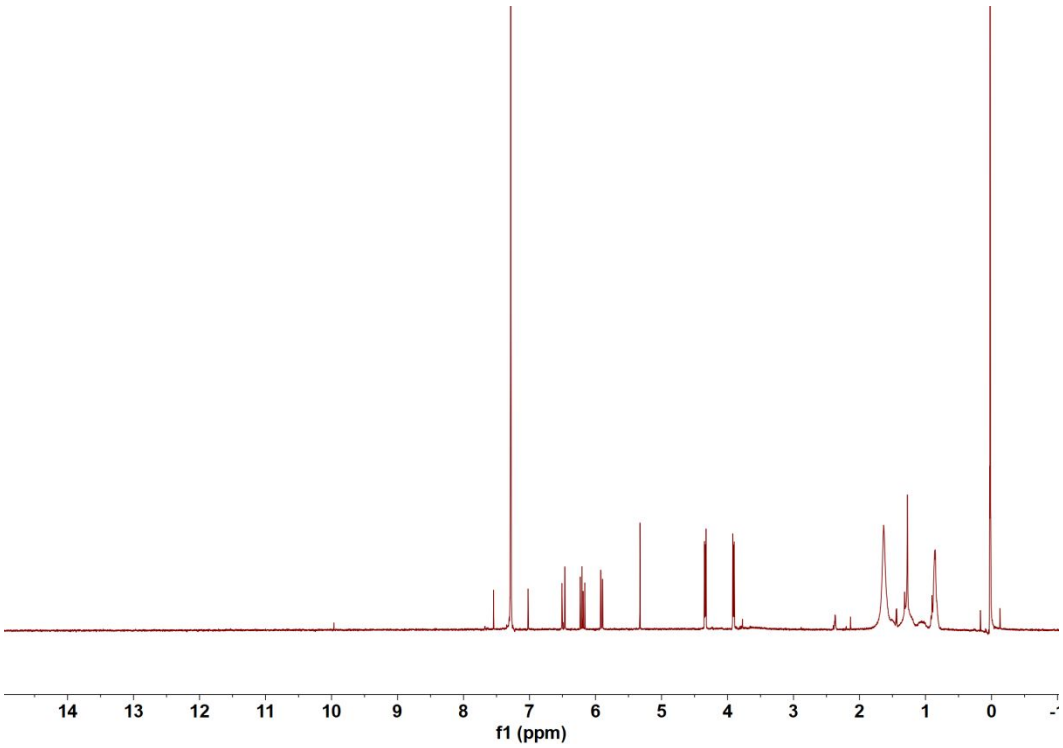


Figure S3. ^{1}H NMR of the product of PyBN/HEA after irradiation of 365-nm LED for 360 s in $CDCl_3$.

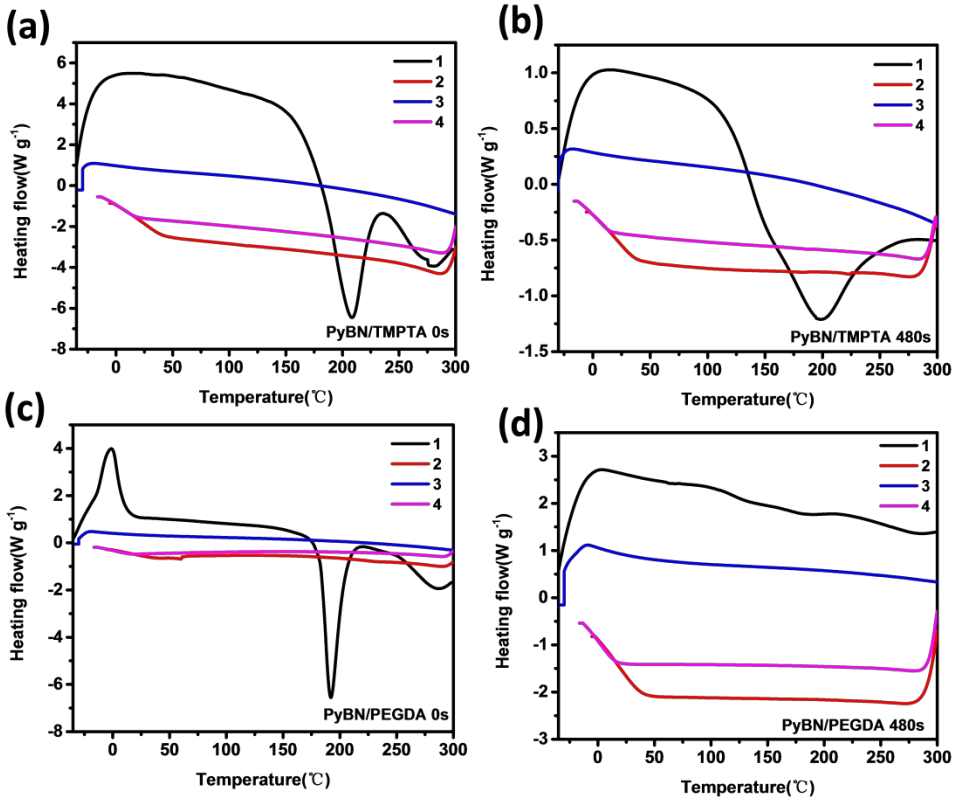


Figure S4. DSC curves of 0.5 wt% PyBN/TMPTA system of irradiation time at (a) 0s and (b) 480s, and DSC curves of 0.5 wt% PyBN/PEGDA system of irradiation time at (c) 0s and (d) 480s.

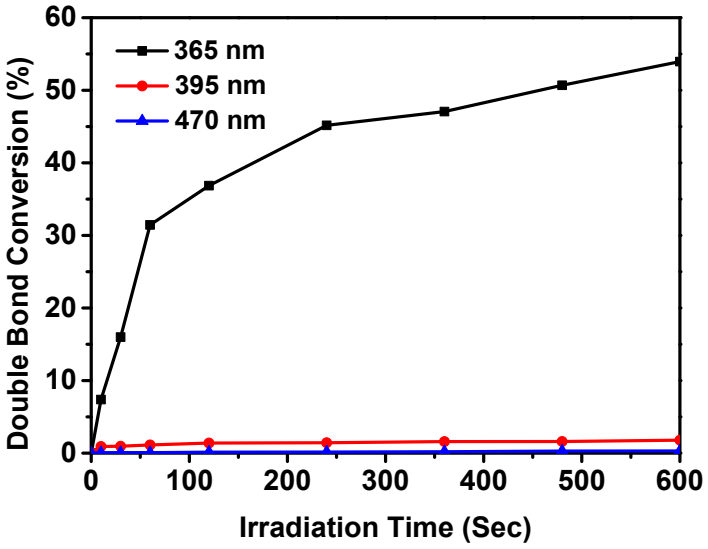
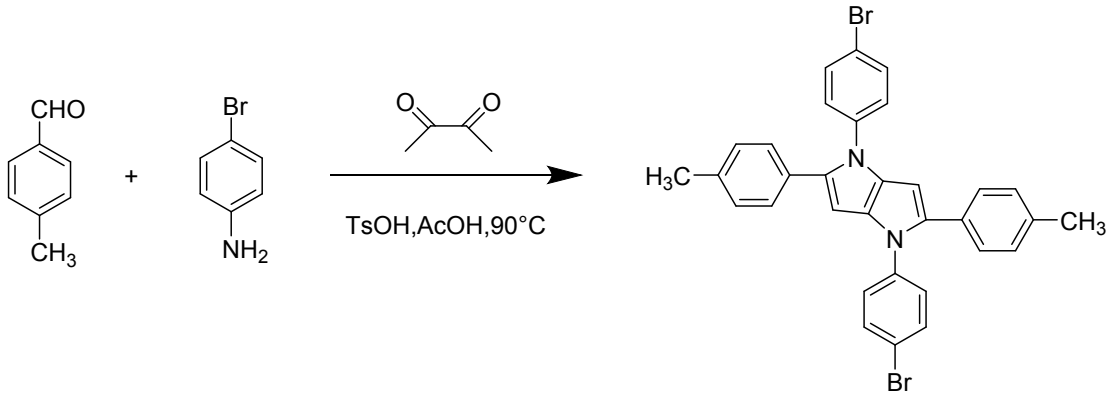


Figure S5. The double bond conversions of the 0.5 wt%PyBN/ TMPTA system under 365nm, 395 nm, and 470 nm LED with the same light intensity of 1.8 mW cm^{-2} and the same condition.



Scheme S1. Synthetic route of PyBC.

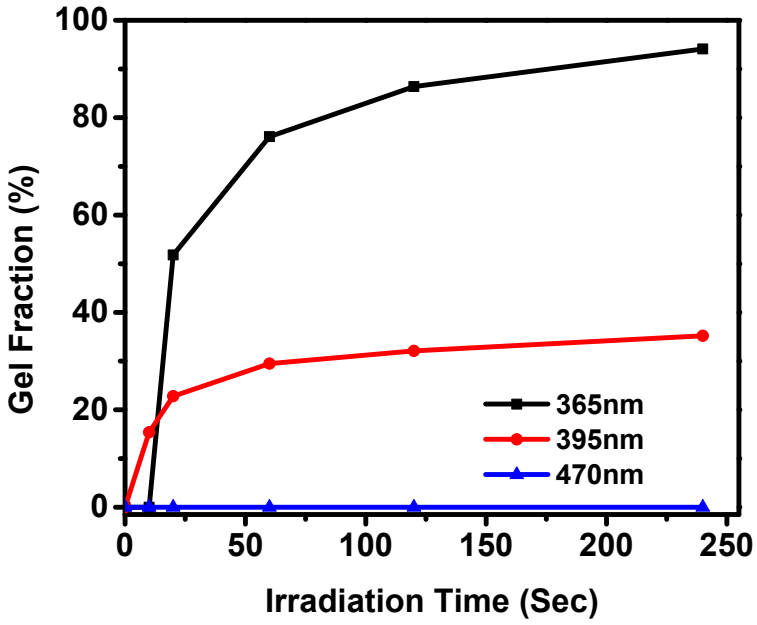


Figure S6. The gel fraction of PyBC/TMPTA at 365nm, 395nm, and 470nm LED under air.

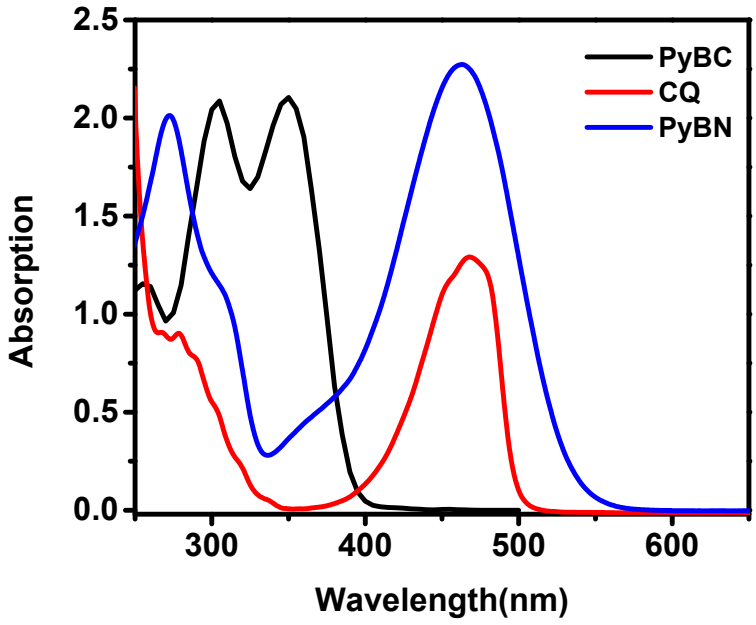


Figure S7. Absorption spectra of PyBN, PyBC, and CQ in CH_2Cl_2. The concentrations of PyBN and PyBC are 5×10^{-6} mol L^{-1}, and that of CQ is 3×10^{-3} mol L^{-1} .

Table S1. Photochemical and electrochemical parameters of PyBN, PyBC, and CQ.

Compound	λ_{max}^{abs}/nm	ε_{max}/L mol^{-1} cm^{-1}	E_{ox}/V [a]	E_{red}/V [b]	E_{00}/eV	ΔG_{el}/eV
PyBN	463	454600	-0.998	1.14	2.40	-2.33
PyBC	350	421000	-0.556	1.86	3.1	-2.59
CQ	468	430	-0.92	-1.064		-

[a] The first oxidation potential value.

[b] The first reduction potential value.

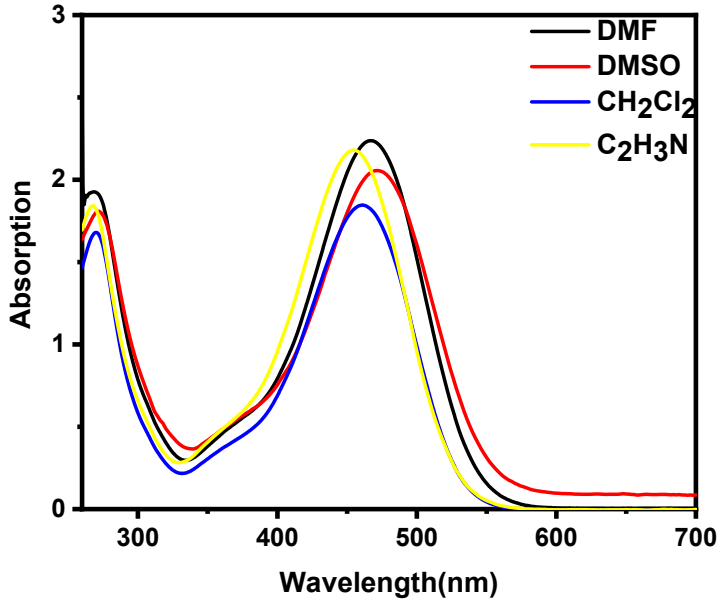


Figure S8. Absorption spectra of PyBN in DMF, DMSO, CH_2Cl_2, and CH_3CN.

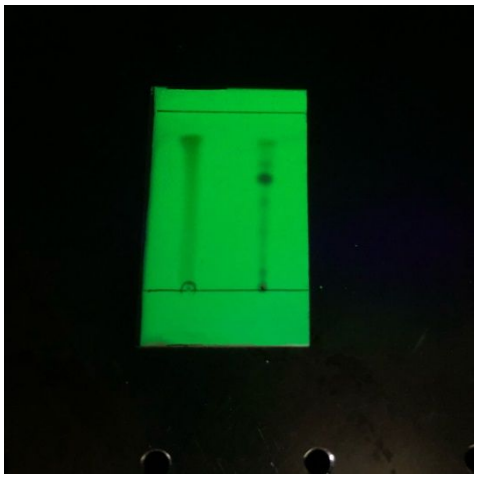
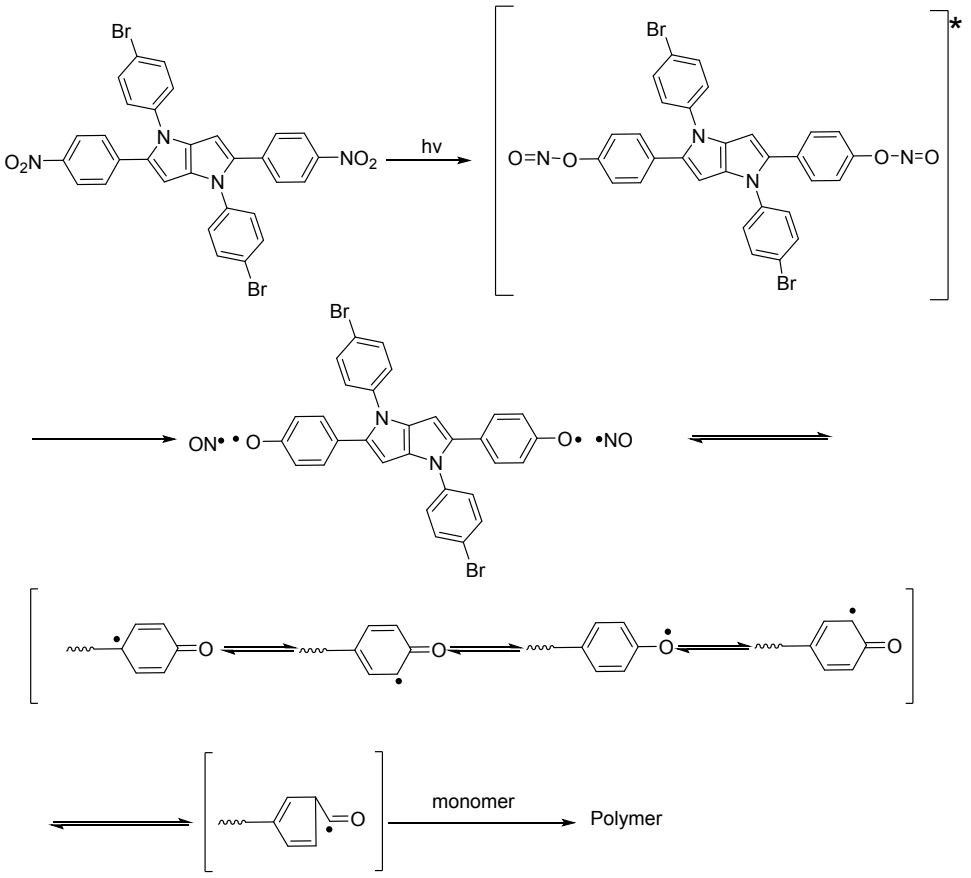


Figure S9. Thin layer chromatography of PyBN (Left) and after photolysis at 480 s under LED irradiation of 365 nm (Right). The developing agent is petrol ether/ethyl acetate with a volume ratio of 2:1.



Scheme S2. Possible mechanism for inducing free-radical photopolymerization by PyBN.

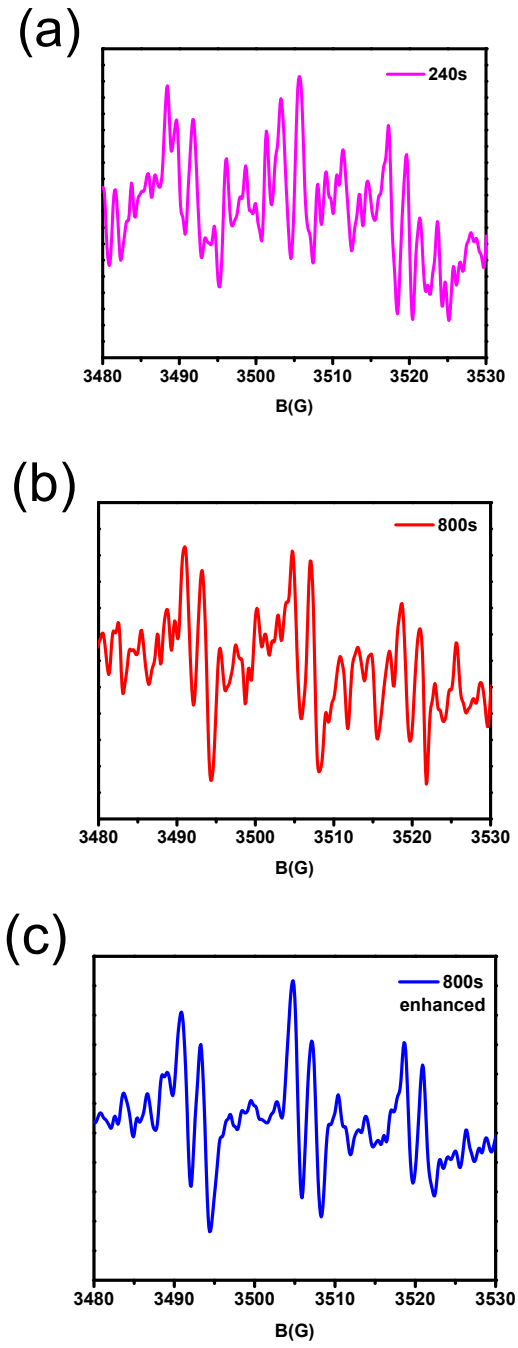


Figure S10. EPR spectra obtained after the irradiation of a PBN solution of PyBN/PBN at 470 nm under argon for (a) 240 s with the power of 2 mW, (b) 800s with the power of 2 mW, and (c) 800s with the enhanced power of 6.325 mW. The light intensity is 110 mW cm^{-2}, and the concentrations of PyBN and PBN are 5×10^{-5} and 5×10^{-2} mol L^{-1}, respectively.

Figure S11. The sample after cured by dual-wavelength photopolymerization.

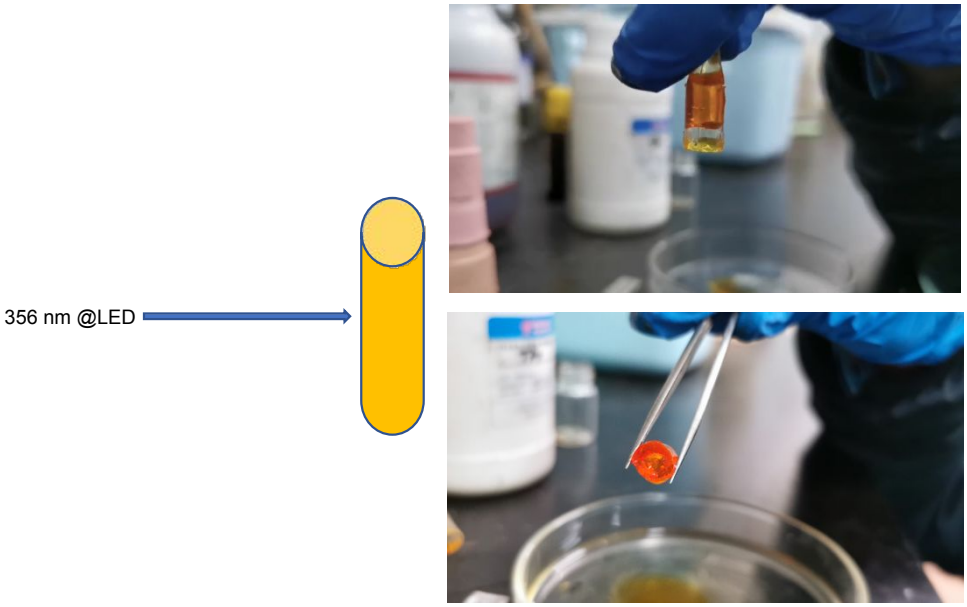
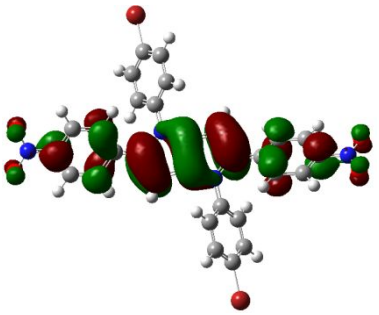
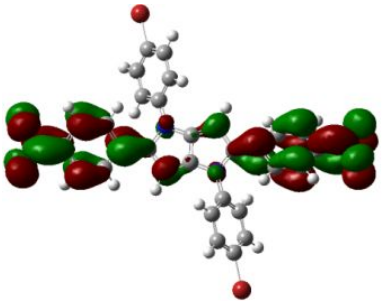


Figure S12. The sample after cured by only 365nm light without 470nm light for comparison.

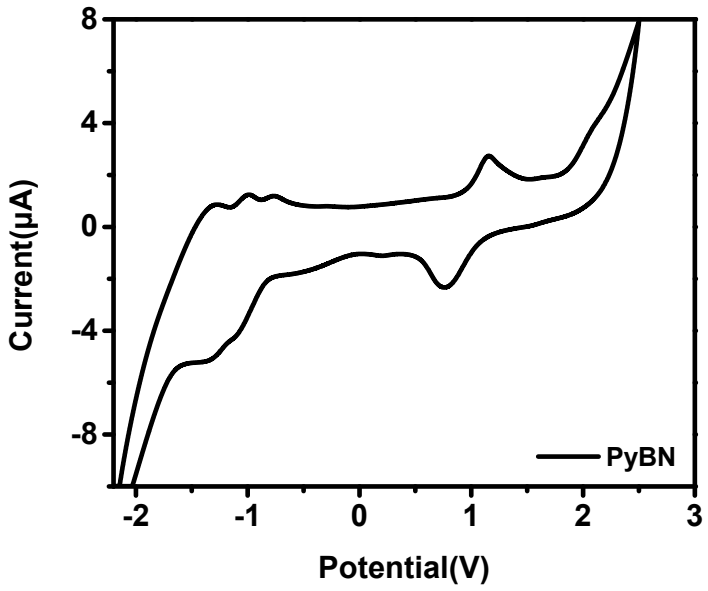


HOMO

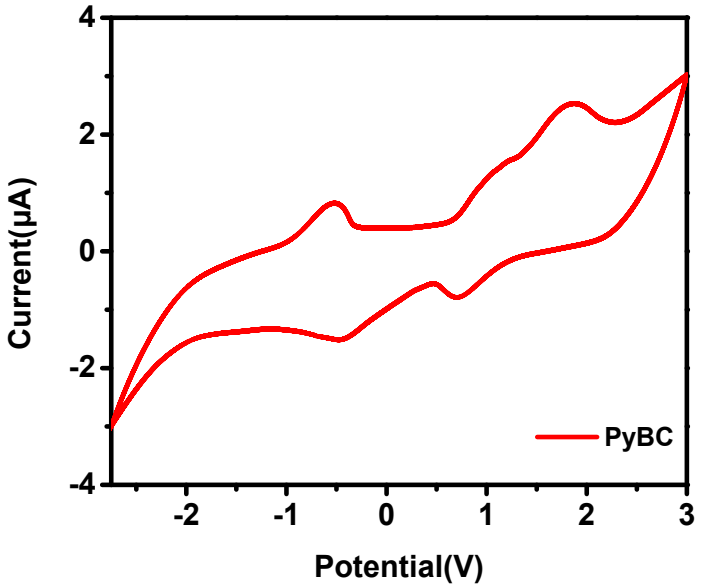


LUMO

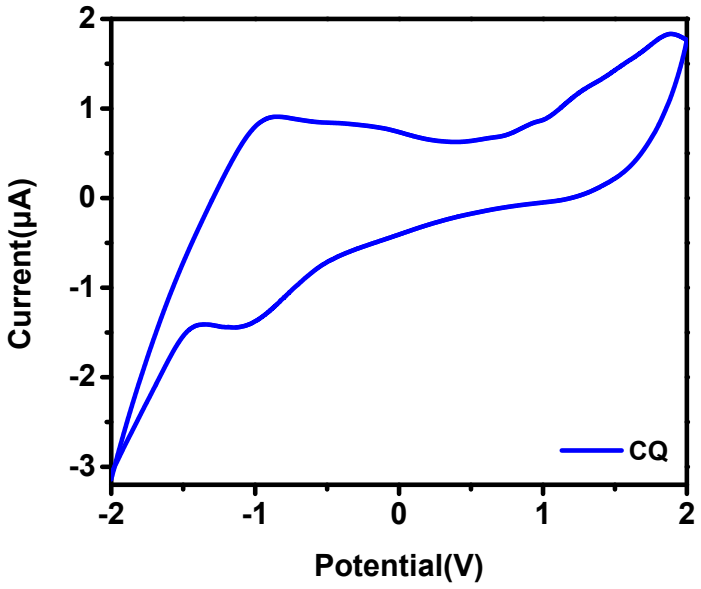
Figure S13. The frontier molecular orbital distributions of PyBN.



(a)

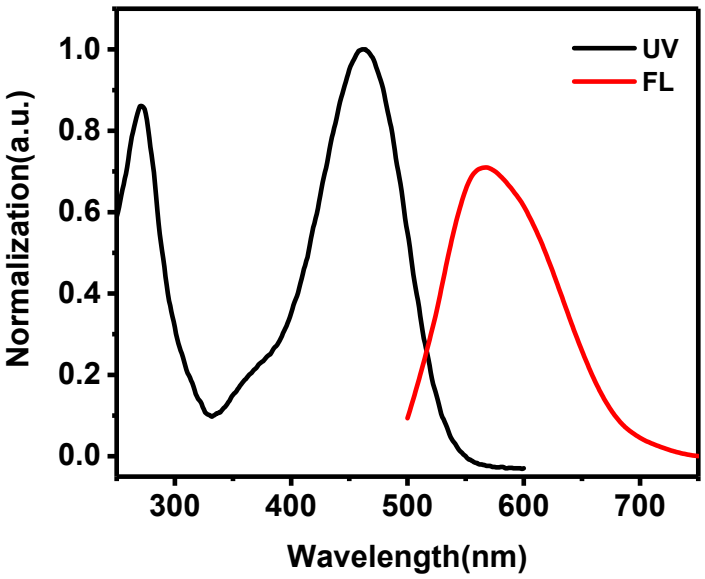


(b)

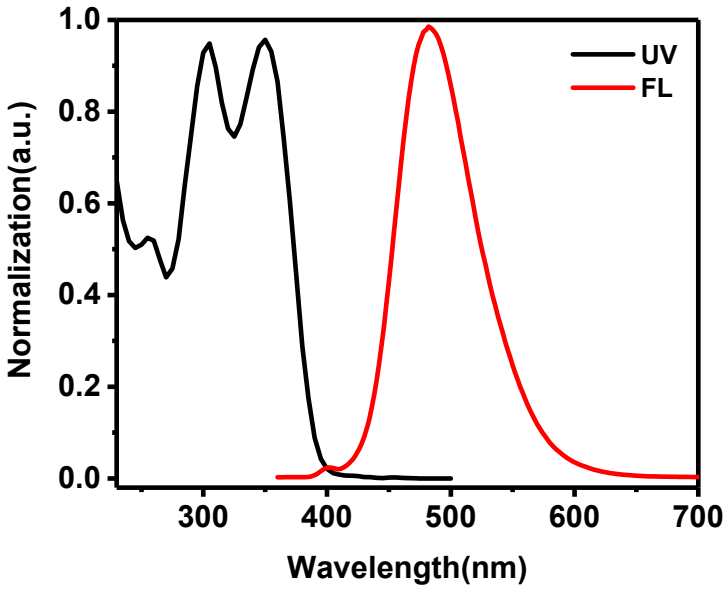


(c)

Figure S14. CV curves of (a) PyBN, (b) PyBC and (c) CQ.



(a)



(b)

Figure S15 Normalized absorption and emission spectra of (a) PyBN and (b) PyBC in CH_2Cl_2.

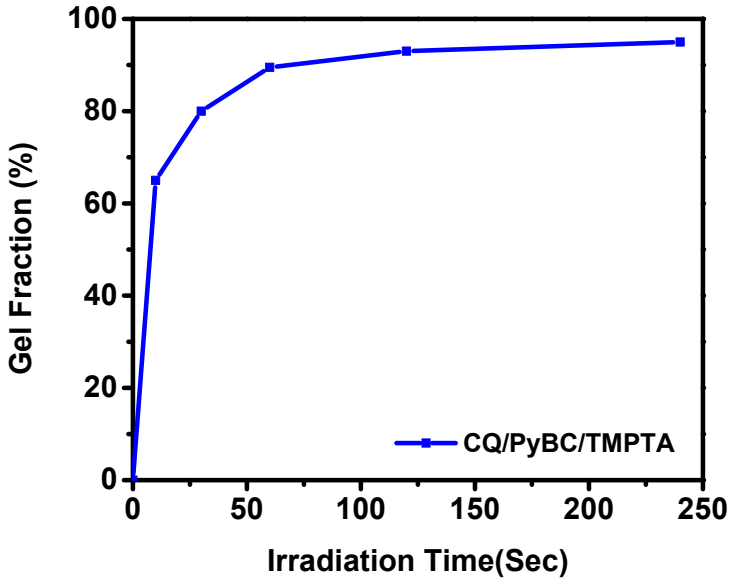


Figure S16. The gel-fraction result of 1.0 wt% CQ/0.5 wt% PyBC/TMPTA under LED irradiator of 470nm in air.

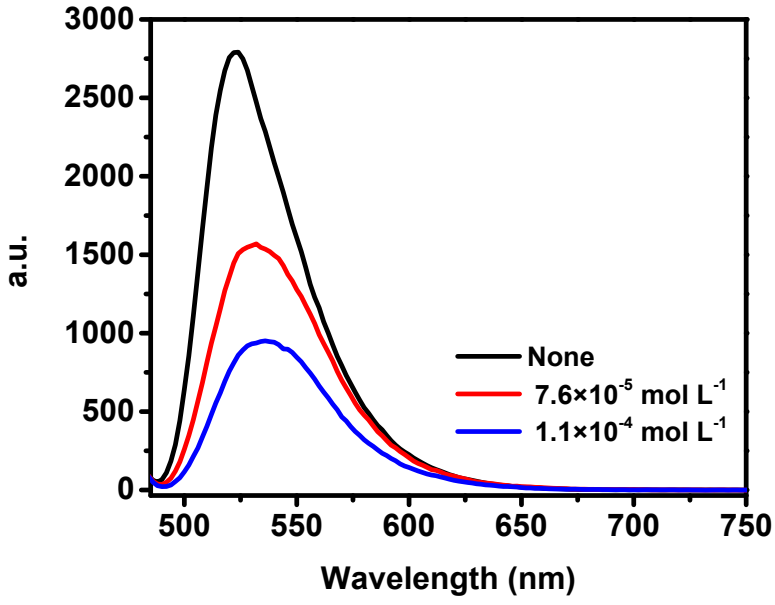


Figure S17. The fluorescence emission spectra of CQ and CQ in the presence of /PyBN in CH_2Cl_2. The concentrations of CQ and PyBN are 7.6×10^{-5} mol L^{-1} and 1.1×10^{-4}mol L^{-1}.

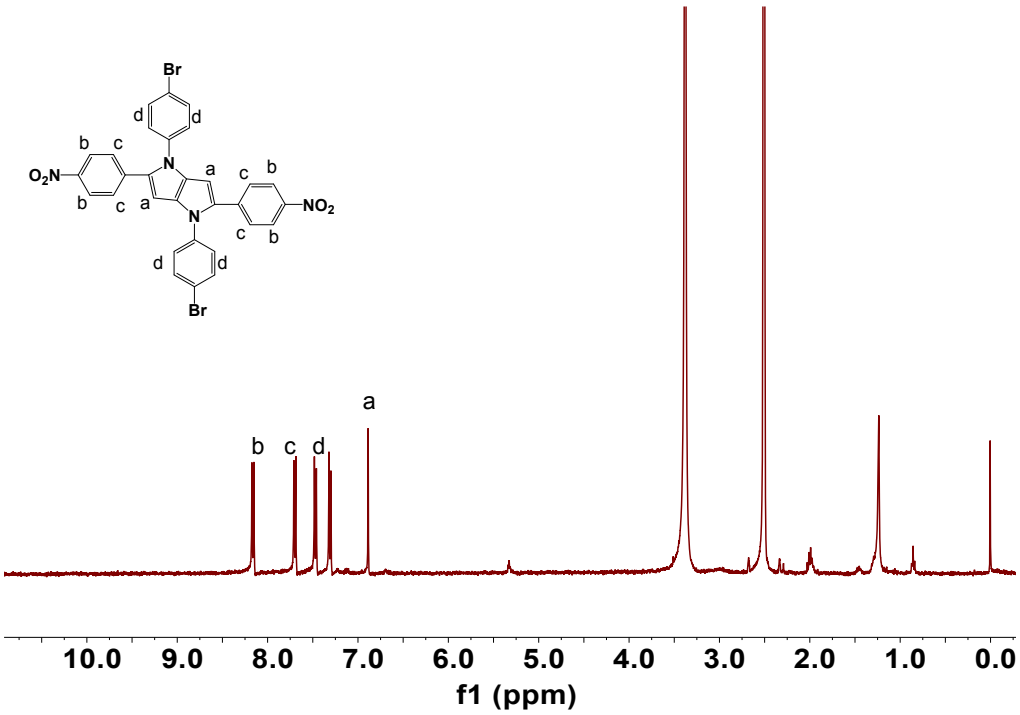


Figure S18. ^{1}H NMR of PyBN in DMSO-d_6. **a**: Signals from the H atom of pyrrole; **b-c:** Signals from H atom on nitrobenzene; **d**:Signals from the H atom of the bromobenzene.

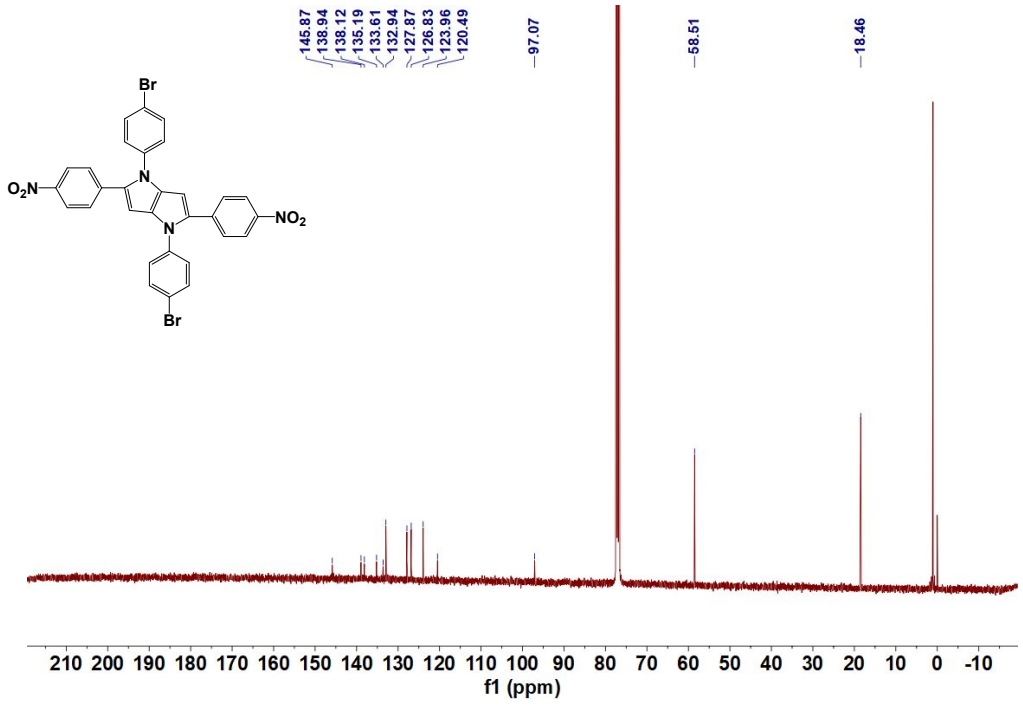


Figure S19. ^{13}C NMR of PyBN in $CDCl_3$.

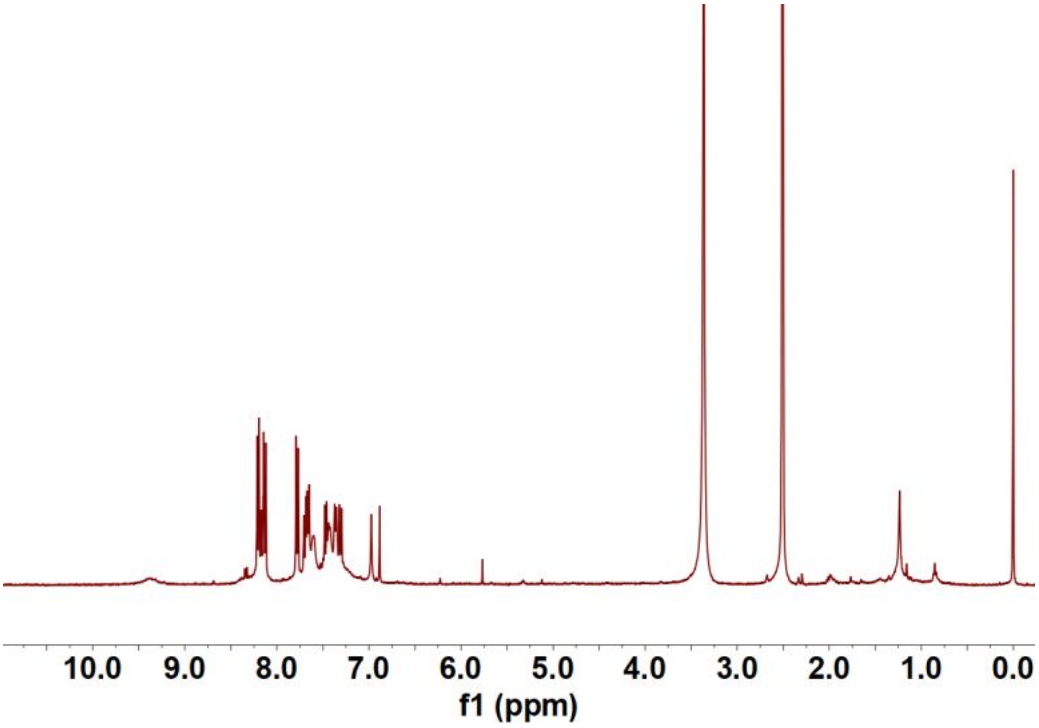


Figure S20. ^{1}H NMR of PyBN in DMSO-d_6 after irradiation of 365-nm LED for 320 s.

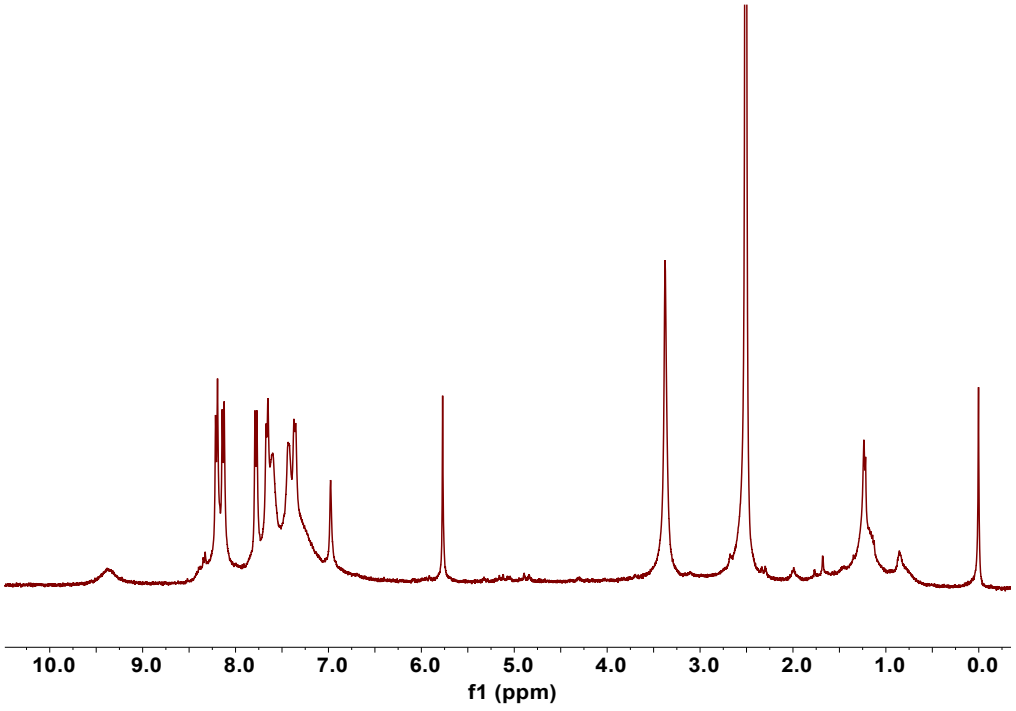


Figure S21. ^{1}H NMR of PyBN in DMSO-d_6 after irradiation of 365-nm LED for 480 s

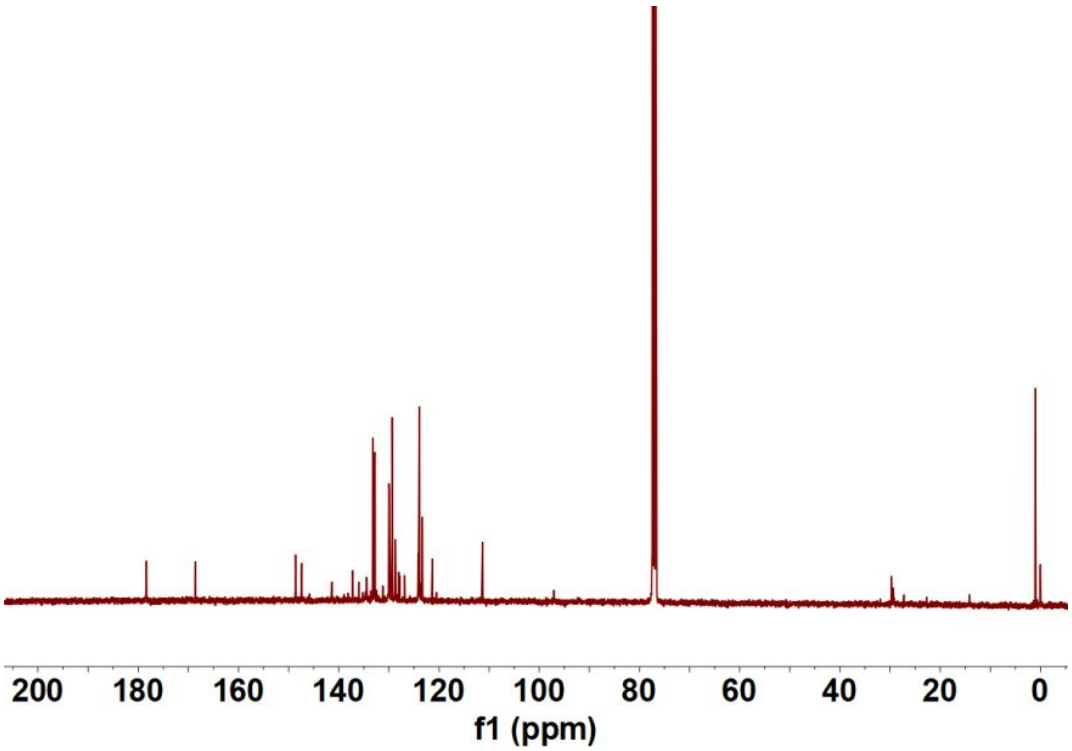


Figure S22. ^{13}C NMR of PyBN in $CDCl_3$ after irradiation of 365-nm LED for 320s

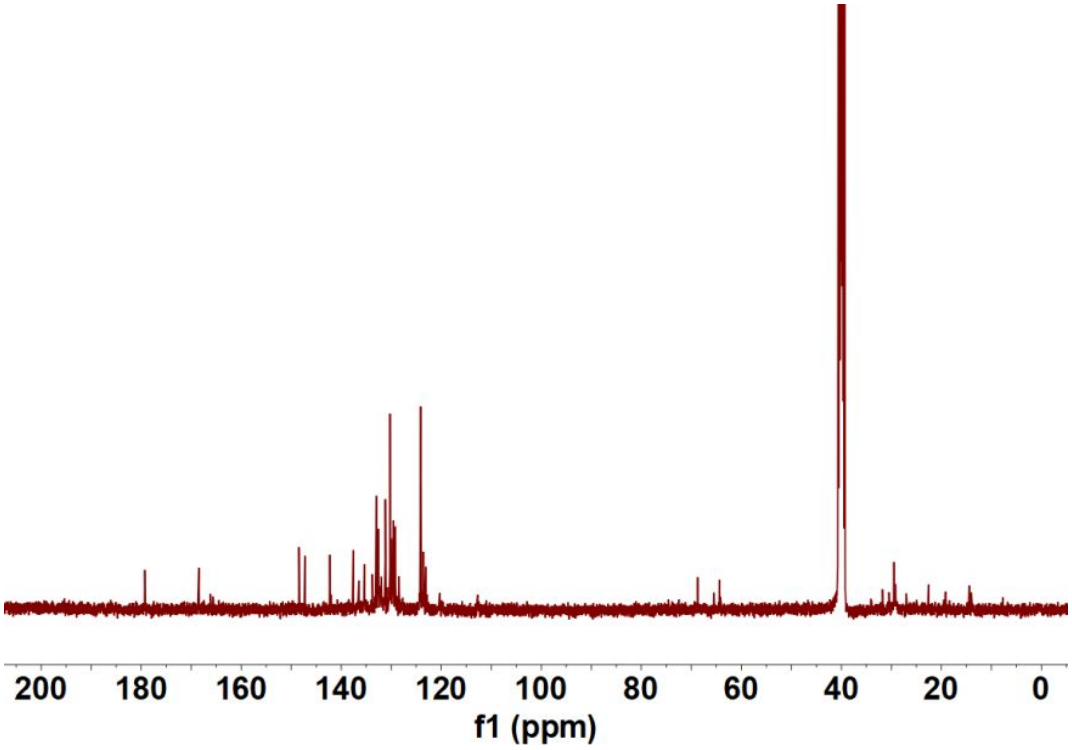


Figure S23.^{13}C NMR of PyBN in DMSO-d_6 after irradiation of 365-nm LED for 480s

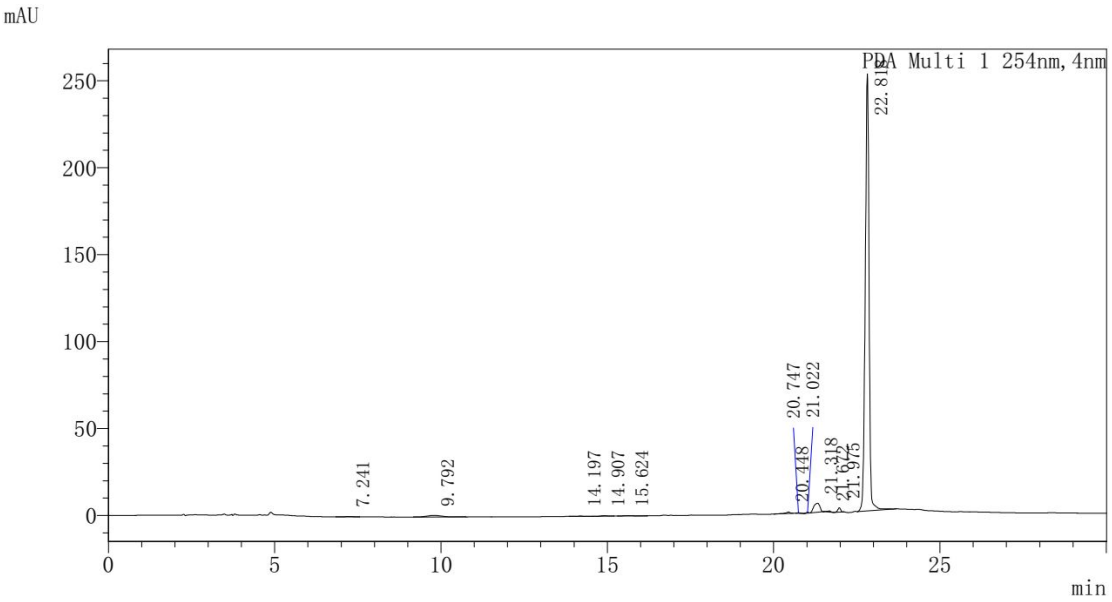


Figure S24. HPLC spectra of PyBN.

Table S2. The HPLC data of PyBN.

Peak	Retention time	Area	Height	Area%
1	7.241	3727	251	0.175
2	9.792	28483	894	1.335
3	14.197	1986	158	0.093
4	14.907	4467	357	0.209
5	15.624	2799	135	0.131
6	20.448	7654	893	0.359
7	20.747	1633	340	0.077
8	21.022	2813	649	0.132
9	21.318	66649	5200	3.123
10	21.672	4525	669	0.212
11	21.975	14415	2474	0.675
12	22.818	1995009	251376	93.480

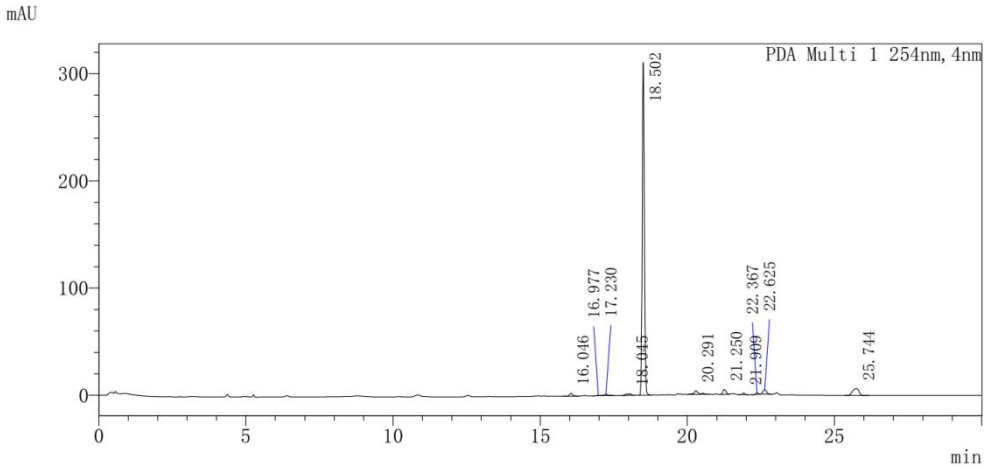
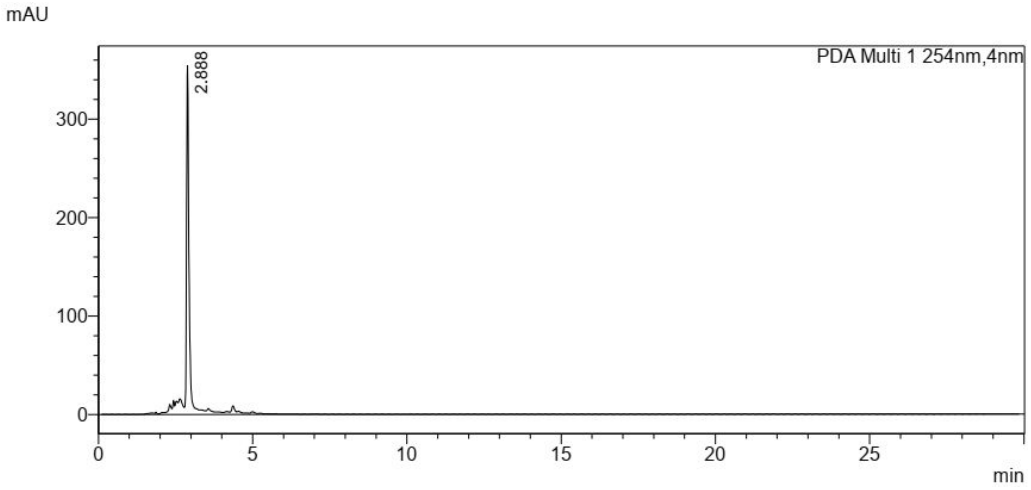


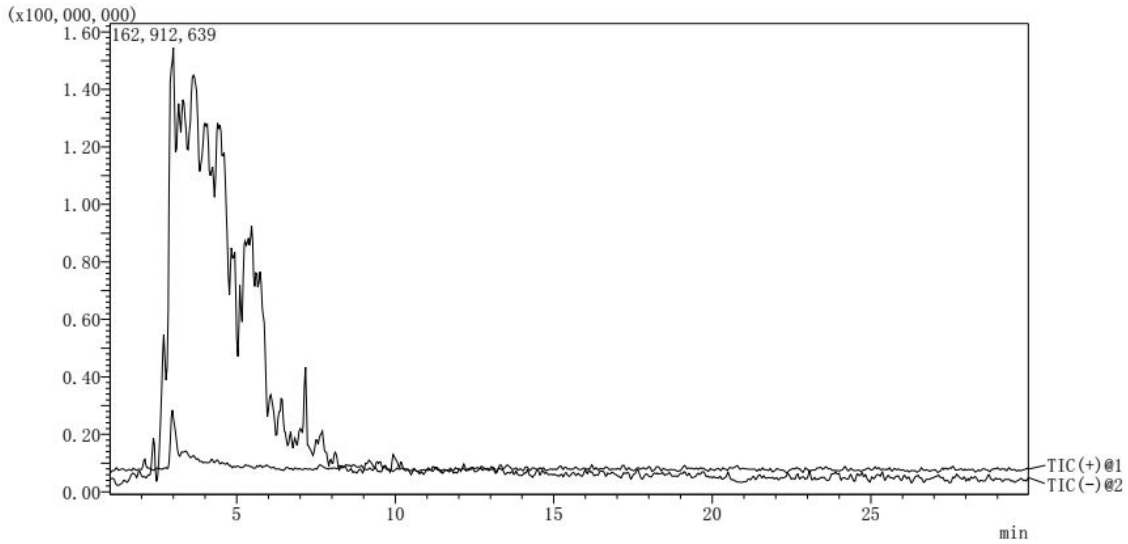
Figure S25. HPLC spectra of the product of PyBN after irradiation of 365-nm LED for 480s.

Table S3. The HPLC data of the product of PyBN after irradiation of 365-nm LED for 480s.

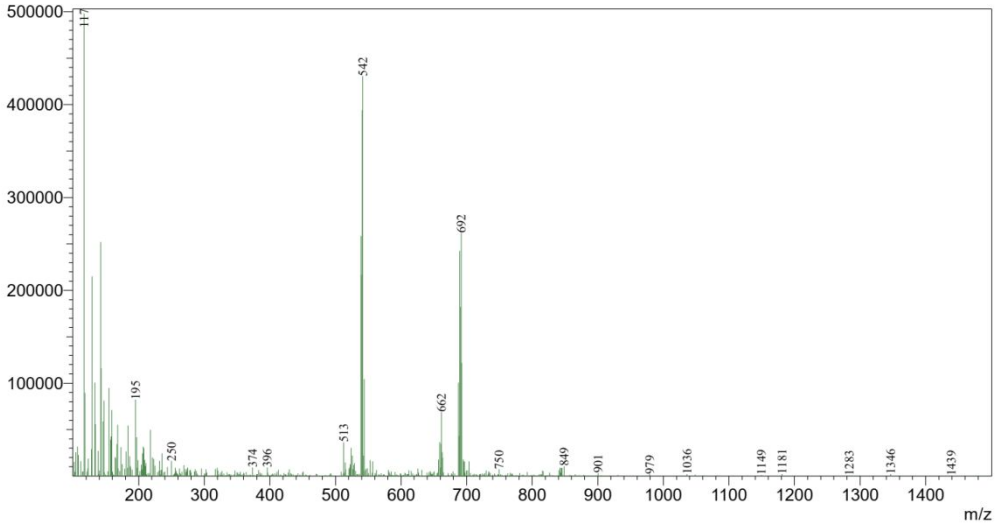
Peak	Retention time	Area	Height	Area%
1	16.046	20417	2666	1.101
2	16.977	2803	352	0.151
3	17.230	12599	1333	0.679
4	18.045	20808	1562	1.122
5	18.502	1582717	310423	85.343
6	20.291	36755	3400	1.982
7	21.250	31847	4490	1.717
8	21.909	7533	1400	0.406
9	22.367	8475	1557	0.457
10	22.625	34947	4035	1.884
11	25.744	95636	6374	5.157


mAU
PDA Multi 1 254nm,4nm
2.888
300
200
100
0
0
5
10
15
20
25
min

(a)


(x100, 000, 000)
162, 912, 639
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
5
10
15
20
25
min
TIC(+)@1
TIC(-)@2

(b)


500000
400000
300000
200000
100000
117
542
692
662
195
250
374
396
513
750
849
901
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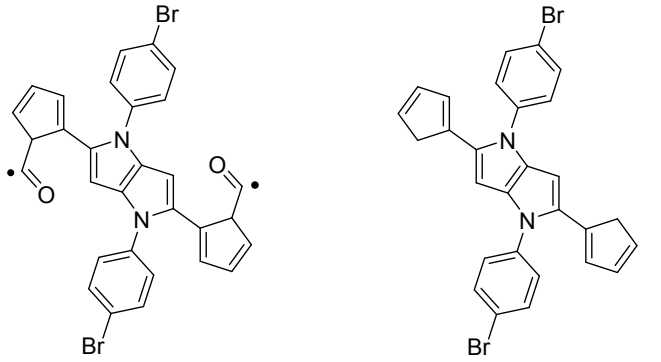
1036
1149
1181
1283
1346
1439
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
m/z

(c)

Figure S26. LC/MS spectra of the main product of PyBN after irradiation of 365-nm LED for 480s. (a) Liquid chromatogram, (b) total ion chromatogram (TIC), and (c)mass spectra ionized in the electrospray ionization(ESI) and operated in negative mode.



main product product fragment m/z=542

Figure S27. The inferred structure of main photolysis product for $C_{30}H_{18}Br_2N_2O_2$ and its mass fragment for $C_{28}H_{20}Br_2N_2$ at m/z=542.

References

(1) Martins, L. M.; Vieira, S. F.; Baldacim, G. B.; Bregadiolli, B. A.; Caraschi, J. C.; Batagin-Neto, A.; Silva-Filho, L. C. Improved synthesis of tetraaryl-1,4-dihydropyrrolo[3,2-b]pyrroles a promising dye for organic electronic devices: An experimental and theoretical approach, *Dyes Pigments* **2018**, *148*, 81−90.