# Electronic Supplementary Information (ESI)

## Modulating the electron-donating ability of aggregation-induced emission molecules for improved photo-responsive property

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different times of white light irradiation.

16. **Fig. S21** Photoconversion from *Z*-form to *E*-one at different times evaluated from $^{1}$H NMR data.

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21. **Table S4** Comparison of similar structures.

**Materials and instruments**

$^{1}$H NMR and $^{13}$C NMR were determined on a 500 MHz Bruker Avance spectrometer with acetonitrile-*d*, *N,N*-dimethylformamide-$d_7$, chloroform-*d*, and dimethyl sulfoxide-$d_6$ as solutions. Mass spectra were determined on the matrix-assisted laser desorption ionization time-of-flight mass spectrometer. The stability of **DOPBYN**, **OPBYN,** and **PBYN** compounds was characterized by thermogravimetric analysis (TGA) (a heating ramp rate of 10 °C/min under $N_2$ condition) and differential scanning calorimetry (DSC) (a scan rate of 10 °C/min from 20 to 300 °C). The photophysical properties of absorption spectra ($5.0 \times 10^{-5}$ M) and photoluminescence (PL) spectra ($5.0 \times 10^{-5}$ M) of **DOPBYN**, **OPBYN,** and **PBYN** in acetonitrile solution were determined with FL-4600 fluorescent spectrophotometer and Cary 500 UV-vis-NIR spectrophotometer, respectively. The single crystal diffraction data for **DOPBYN**, **OPBYN,** and **PBYN** were tested on the Bruker Apex II CCD diffractometer at 173 K. The crystals were analyzed by OLEX2 software. The excited state lifetimes under the solid of three compounds were measured with the Edinburgh FLSP920 fluorescence spectrophotometer. In the photo-response experiment, the light sources were ZF-5 portable UV analyzer (6 W) and white light LED mining lamp (200 W).

**Scheme S1** Molecular structure and synthesis route of **PBYN**, **OPBYN** and **DOPBYN** molecules.

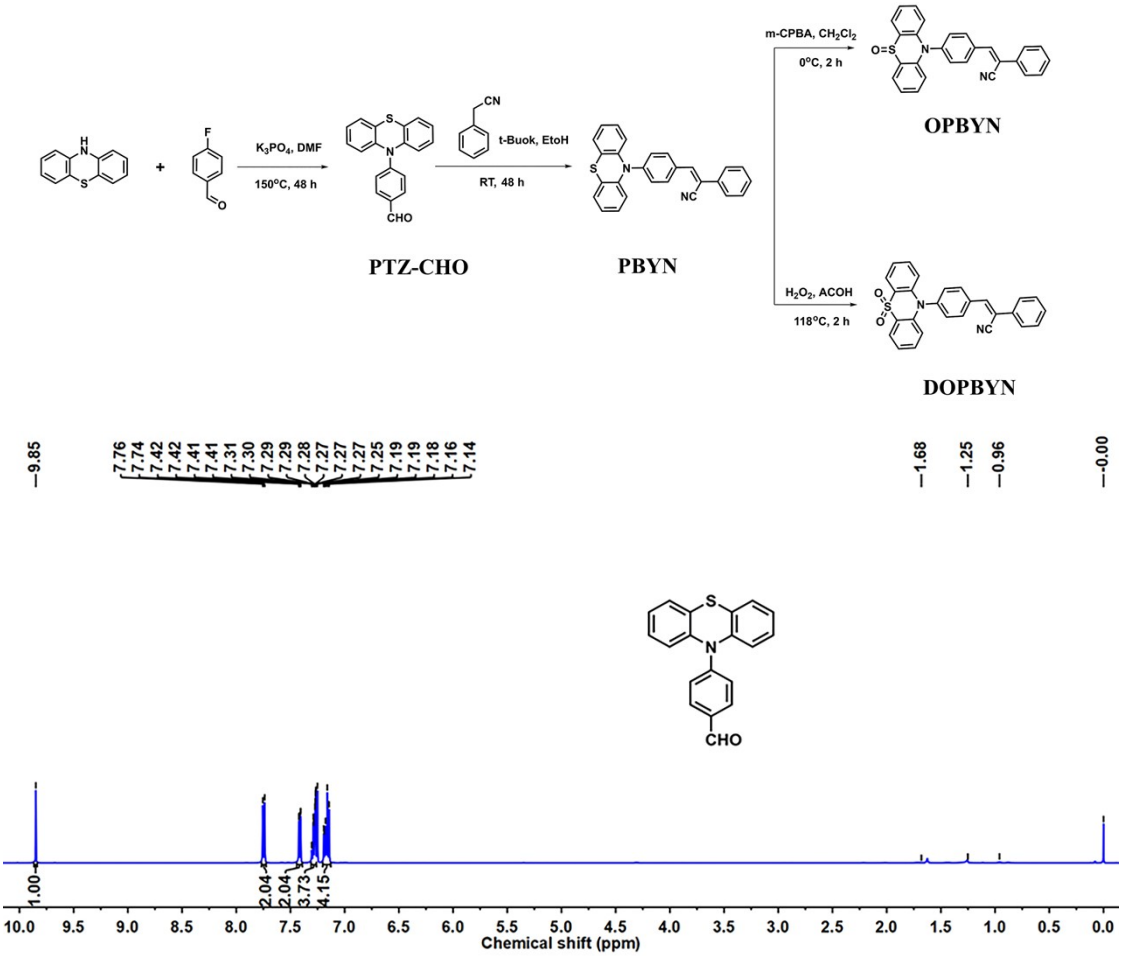



**Fig. S1** $^1$H NMR spectrum of **PTZ-CHO** in DMSO-$d_6$.

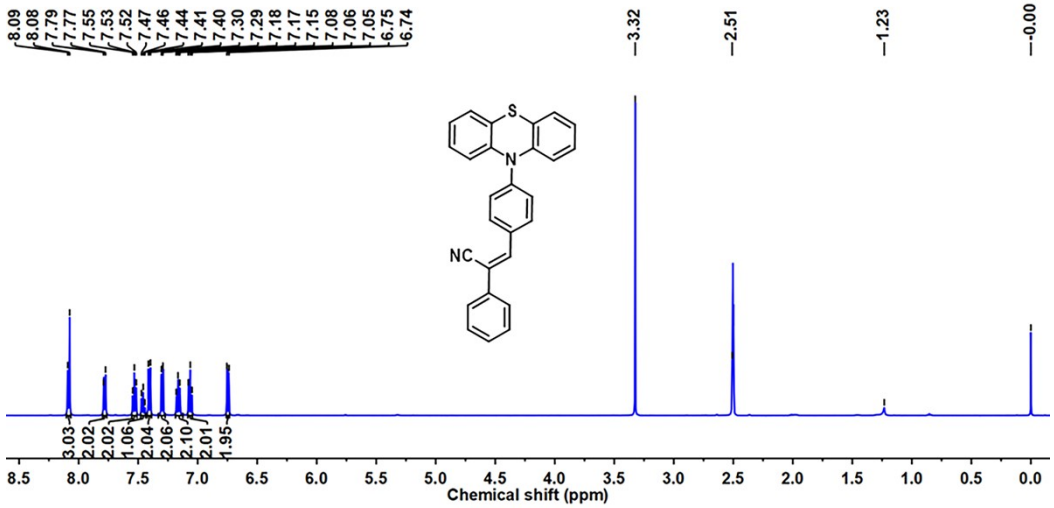



**Fig. S2** $^1$H NMR spectrum of **PBYN** in DMSO-$d_6$.

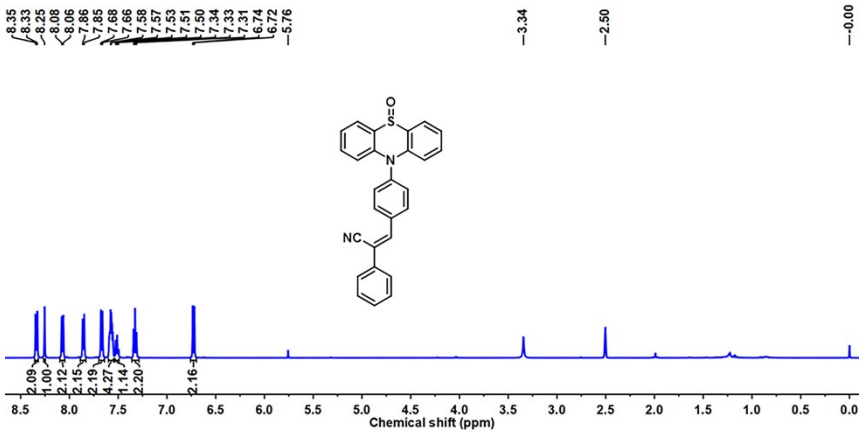



**Fig. S3** $^{1}$H NMR spectrum of **OPBYN** in DMSO-$d_6$.

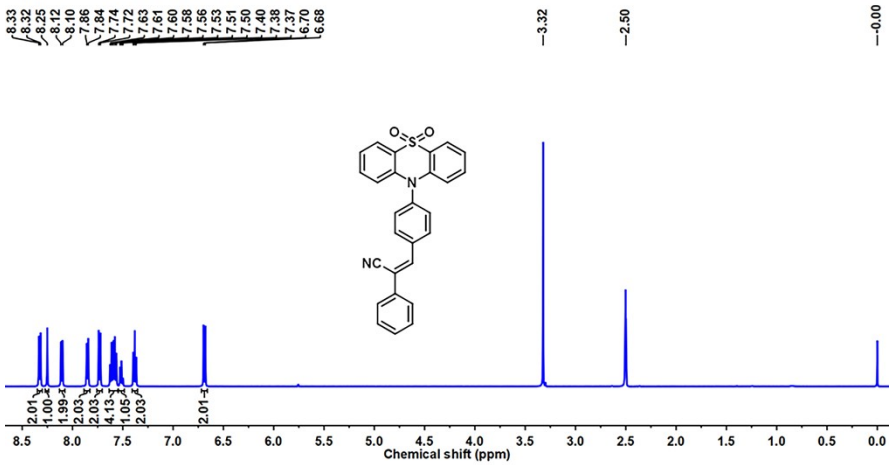



**Fig. S4** $^{1}$H NMR spectrum of **DOPBYN** in DMSO-$d_6$.

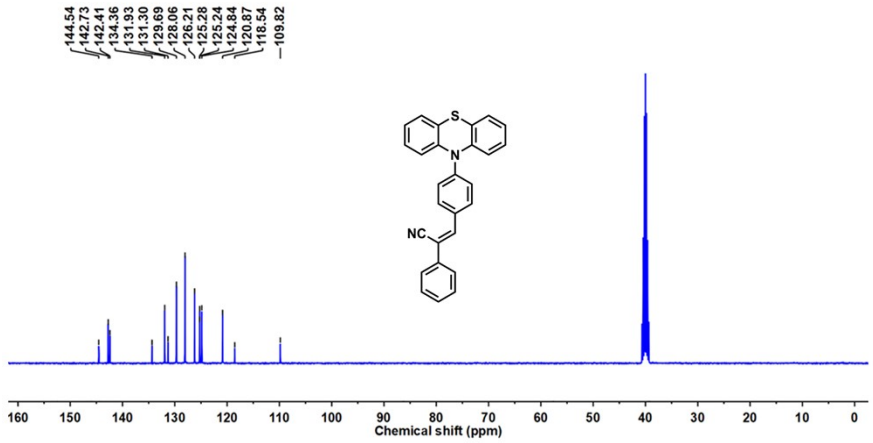



**Fig. S5** $^{13}$C NMR spectrum of **PBYN** in DMSO-$d_6$.

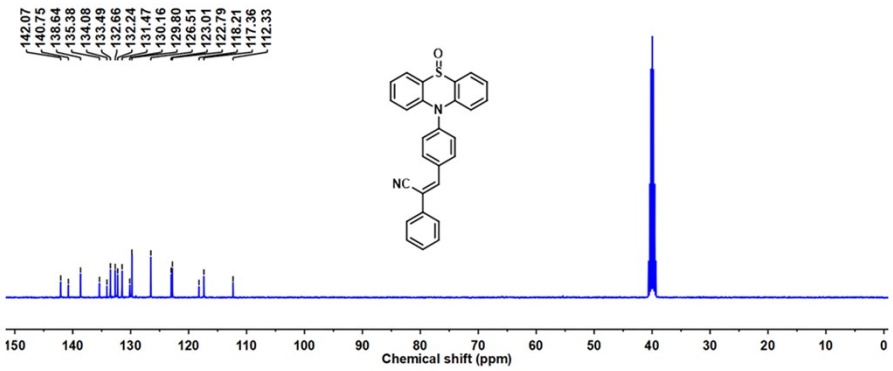



**Fig. S6** $^{13}$C NMR spectrum of **OPBYN** in DMSO-$d_6$.

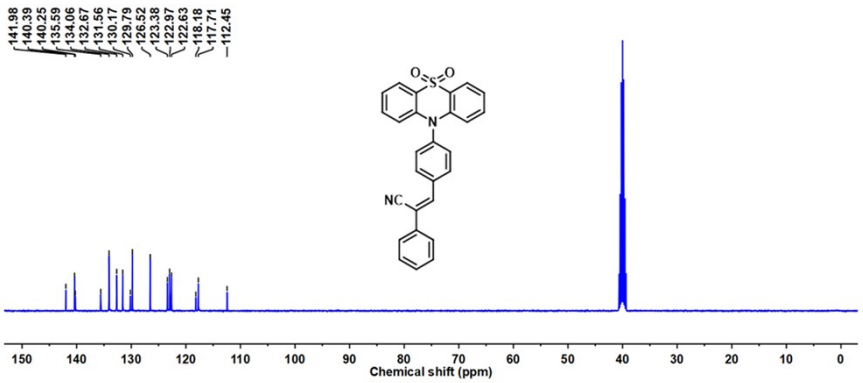



**Fig. S7** $^{13}$C NMR spectrum of **DOPBYN** in DMSO-$d_6$.

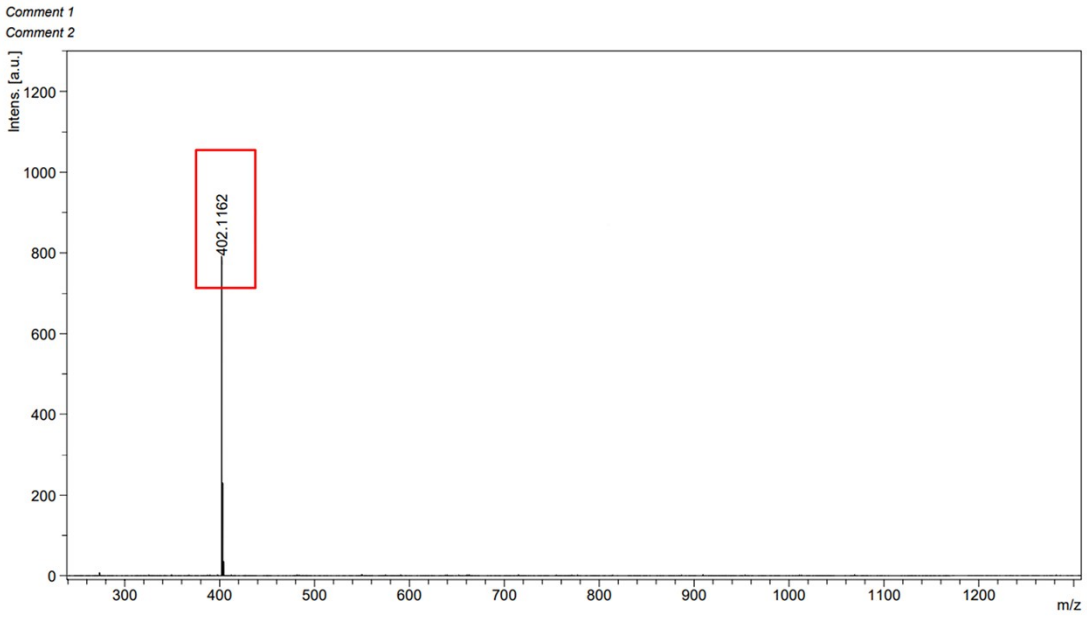



**Fig. S8** High resolution mass spectrum of **PBYN** in $CH_3CN$ solution before light irradiation.

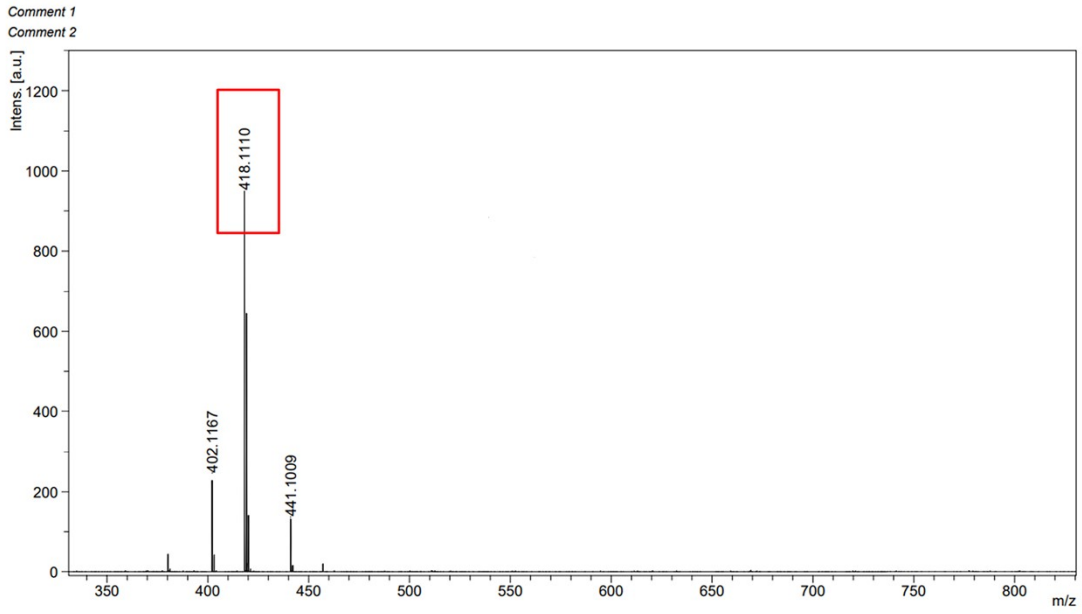



**Fig. S9** High resolution mass spectrum of **OPBYN** in $CH_3CN$ solution before light irradiation.

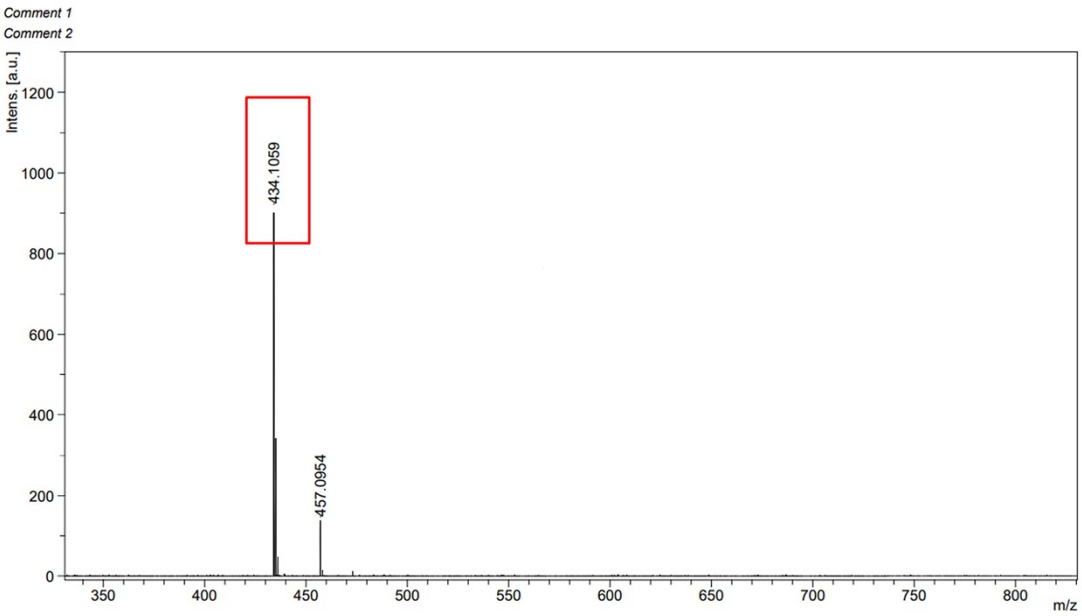



**Fig. S10** High resolution mass spectrum of **DOPBYN** in $CH_3CN$ solution before light irradiation.

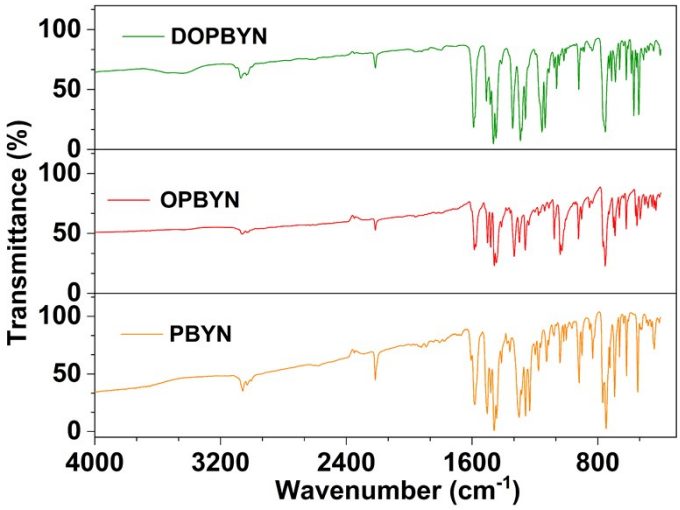



**Fig. S11** Infrared spectra of **DOPBYN**, **OPBYN**, and **PBYN**.

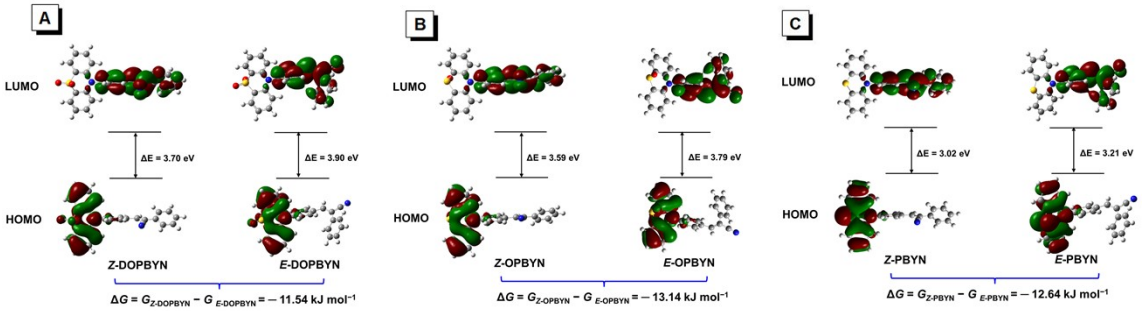



**Fig. S12** The electron density distribution and Gibbs free energies of *Z*-isomer and *E*-one for (A) **DOPBYN**, (B) **OPBYN** and (C) **PBYN**.

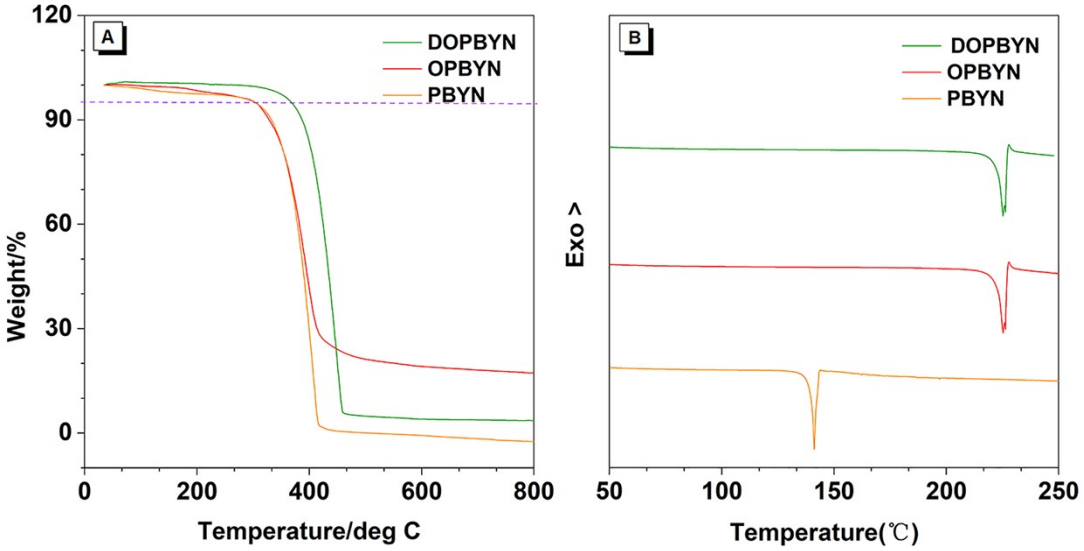



**Fig. S13** (A) TGA and (B) DSC measurements of **DOPBYN**, **OPBYN** and **PBYN**.

**Table S1** Crystal data and refinement parameters for designed compounds.

| Parameter | **PBYN** | **OPBYN** | **DOPBYN** |
|---|---|---|---|
| Formula | $C_{27}H_{18}N_2S$ | $C_{27}H_{18}N_2OS$ | $C_{27}H_{18}N_2O_2S$ |
| Formula weight /g mol$^{-1}$ | 402.49 | 418.49 | 434.49 |
| Temperature/K | 173.0 | 173.0 | 173.0 |
| Crystal system | orthorhombic | orthorhombic | triclinic |
| Space group | Pbca | Pbca | P-1 |
| a/Å | 7.8395(2) | 7.8600(3) | 8.0016(3) |
| b /Å | 15.8248(4) | 16.4878(6) | 8.5097(4) |
| c /Å | 31.9711(8) | 31.1694(11) | 17.1865(7) |
| α /° | 90 | 90 | 80.156(2) |
| β /° | 90 | 90 | 80.347(2) |
| γ /° | 90 | 90 | 67.154(2) |
| Volume /Å$^3$ | 3966.29(17) | 4039.4(3) | 1055.93(8) |
| Z | 8 | 8 | 2 |
| Density, calcd/g cm$^{-3}$ | 1.348 | 1.376 | 1.367 |
| μ/mm$^{-1}$ | 1.564 | 1.596 | 1.584 |
| F(000) | 1680.0 | 1744.0 | 452.0 |
| Reflection, collected | 15470 | 20030 | 16448 |
| $R_{int}$ | 0.0290 | 0.0374 | 0.0587 |
| GOF on $F^2$ | 1.090 | 1.097 | 1.047 |
| $R_1$[a], $wR_2$[b][I>2σ(I)] | 0.0333, 0.0820 | 0.0390, 0.0949 | 0.0551, 0.1416 |
| $R_1$, $wR_2$ (all data) | 0.0380, 0.0846 | 0.0417, 0.0967 | 0.0676, 0.1498 |

[a]$R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b]$wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)]^{1/2}$

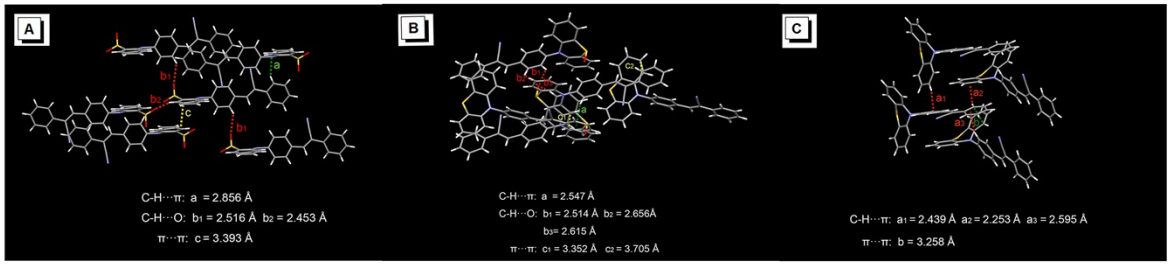



**Fig. S14** Molecular stacking of (A) **DOPBYN**, (B) **OPBYN**, and (C) **PBYN**.

**Table S2** Molecular stacking distance of designed compounds

| Compound/ Molecular stacking | C-H···π (Å) | π···π (Å) | C-H···O (Å) |
|---|---|---|---|
| **DOPBYN** | 2.856 | 3.393 | 2.453/2.516 |
| **OPBYN** | 2.547 | 3.352/3.705 | 2.514/2.615/2.656 |
| **PBYN** | 2.439/2.253/2.595 | 3.258 | – |

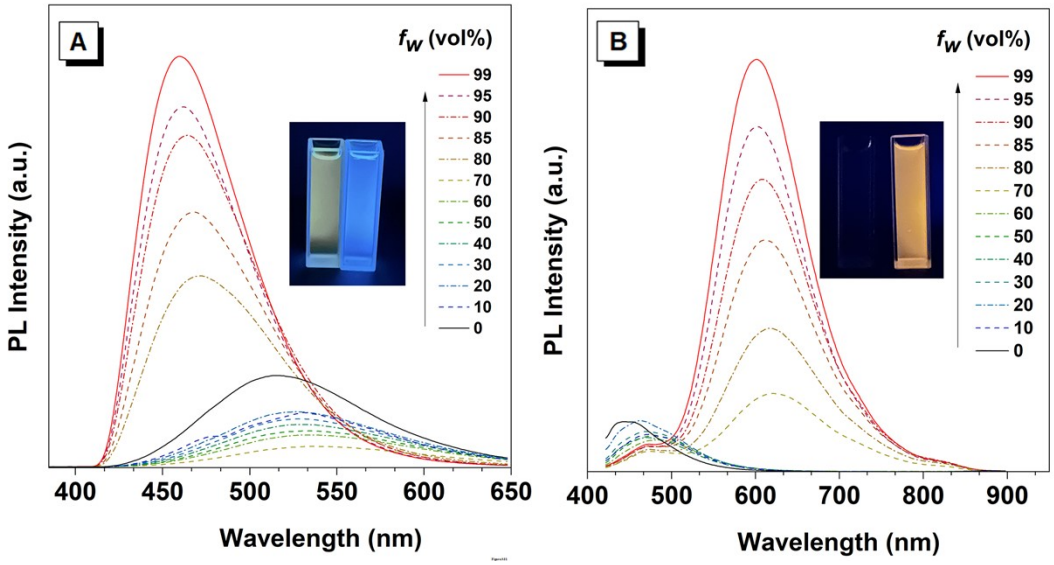



**Fig. S15** PL spectra of (A) **DOPBYN** and (B) **PBYN** in $CH_3CN/H_2O$ solution ($5 \times 10^{-5}$ M) with different water fractions ($f_w$), respectively. Insets in (A) and (B) were the contrast images at 0% and 99%.

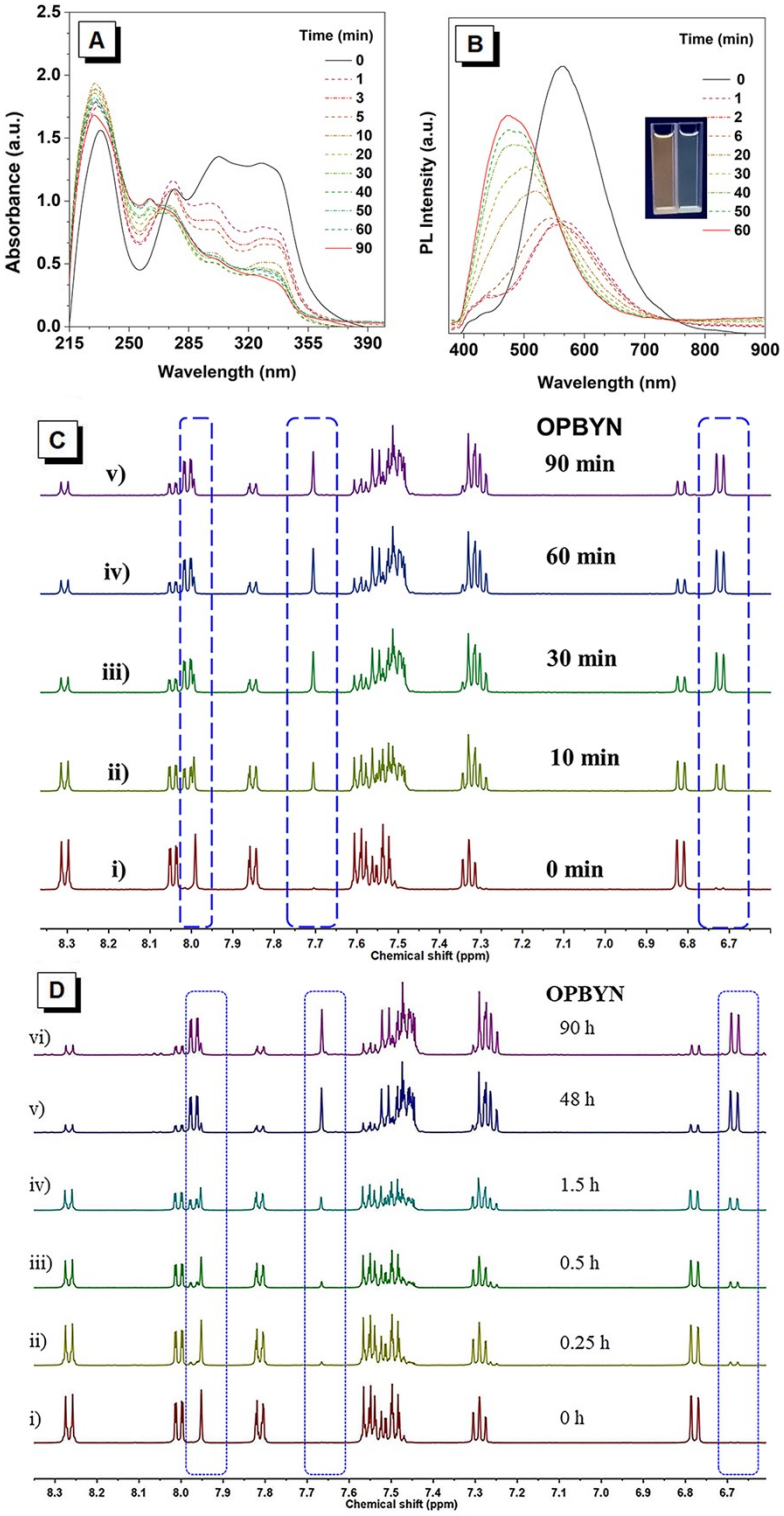



**Fig. S16** (A) UV−vis absorption and (B) PL spectra of **OPBYN** ($5 \times 10^{-5}$ M) in $CH_3CN$ solution with continuous irradiation. (C) $^1H$ NMR spectra of **OPBYN** in $CD_3CN$ solution (3.5 mM) upon exposure duration 365 nm UV light. (D) $^1H$ NMR spectra of **OPBYN** in $CD_3CN$ solution (3.5 mM) upon exposure duration white light.

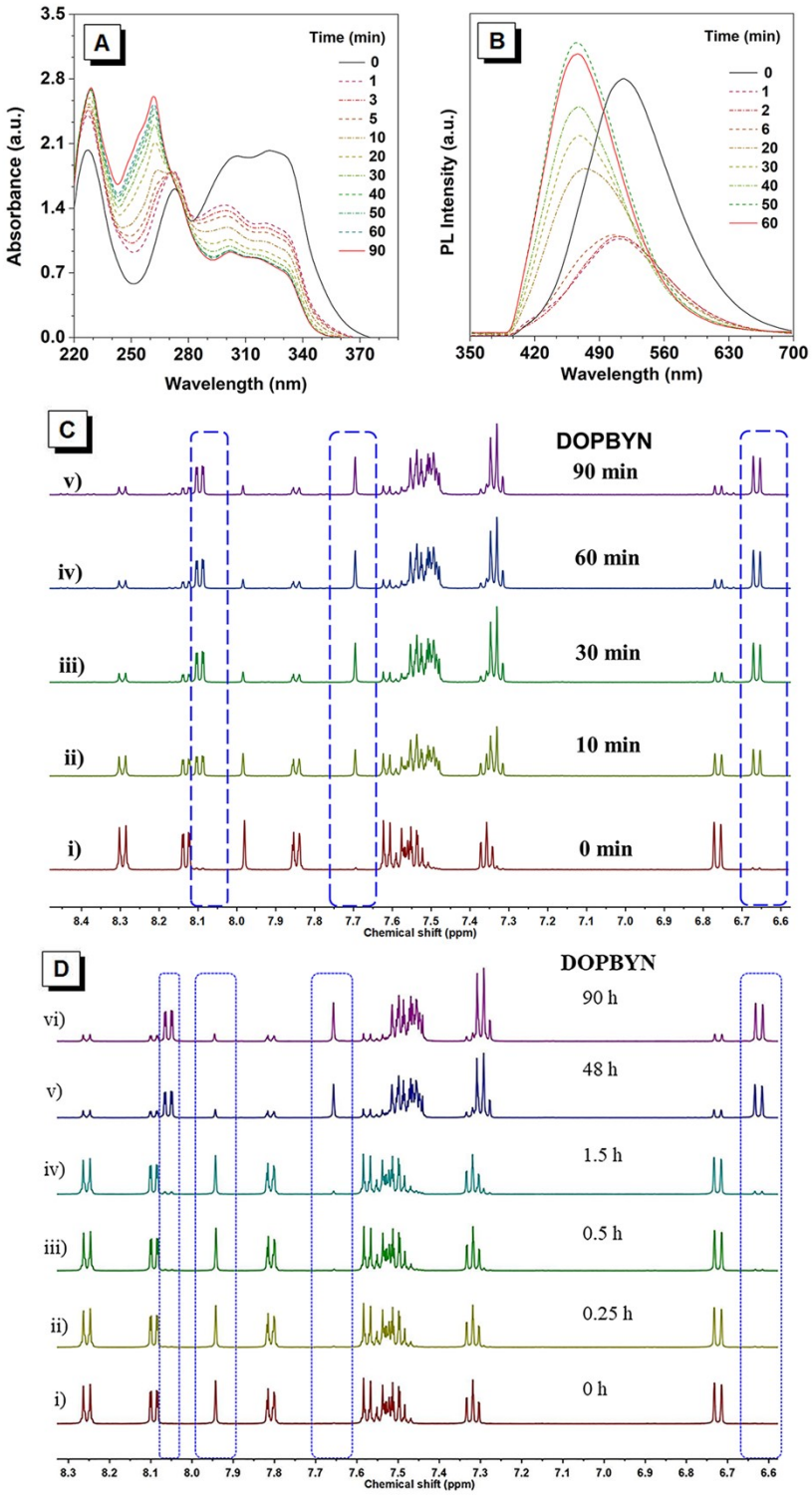



**Fig. S17** (A) UV−vis absorption and (B) PL spectra of **DOPBYN** ($5 \times 10^{-5}$ M) in $CH_3CN$ solution with continuous irradiation. (C) $^1H$ NMR spectra of **DOPBYN** in $CD_3CN$ solution (3.5 mM) upon exposure duration 365 nm UV light. (D) $^1H$ NMR spectra of **DOPBYN** in $CD_3CN$ solution (3.5 mM) upon exposure duration white light.

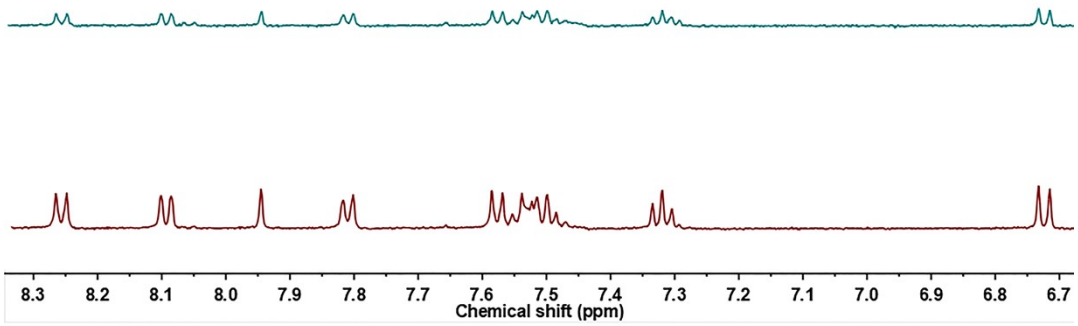



**Fig. S18** $^{1}$H NMR spectrum of pure acetonitrile solution of **DOPBYN** molecule placed in dark room for 12 days.

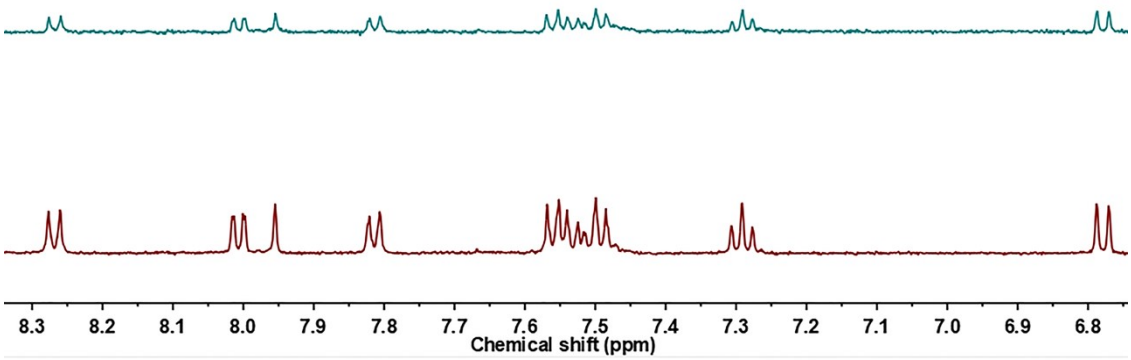



**Fig. S19** $^{1}$H NMR spectrum of pure acetonitrile solution of **OPBYN** molecule placed in dark room for 12 days.

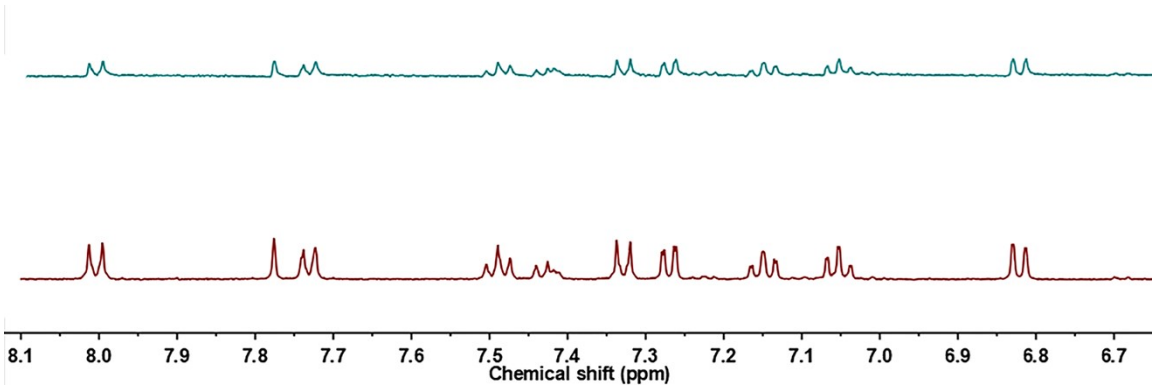



**Fig. S20** $^{1}$H NMR spectrum of pure acetonitrile solution of **PBYN** molecule placed in dark room for 12 days.

**Table S3** Photoconversion of **DOPBYN**, **OPBYN** and **PBYN** molecules at different times of white light irradiation.

| **Compounds/Time** (h) | 0 | 0.25 | 0.5 | 1.5 | 48 | 90 |
|---|---|---|---|---|---|---|
| ***E*-DOPBYN** | 0% | 0% | 3.8% | 8.2% | 81.0% | 81.0% |
| ***E*-OPBYN** | 0% | 7.4% | 16.0% | 37.0% | 81.0% | 82.3% |
| ***E*-PBYN** | 0% | 43.0% | 50.0% | 81.0% | 81.0% | 89.6% |

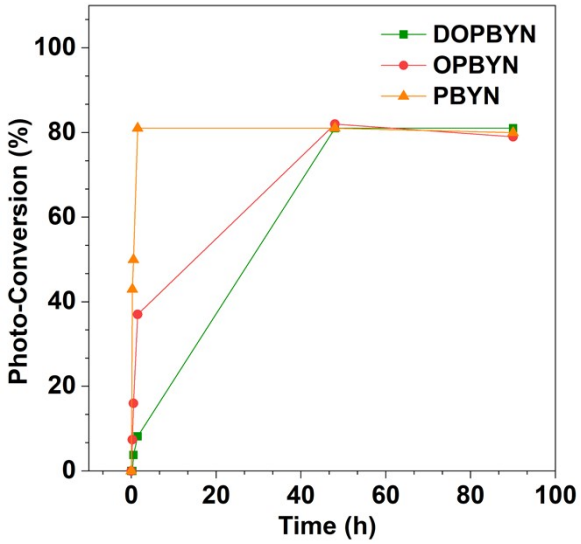



**Fig. S21** Photoconversion from *Z*-form to *E*-one at different times evaluated from $^{1}$H NMR data.

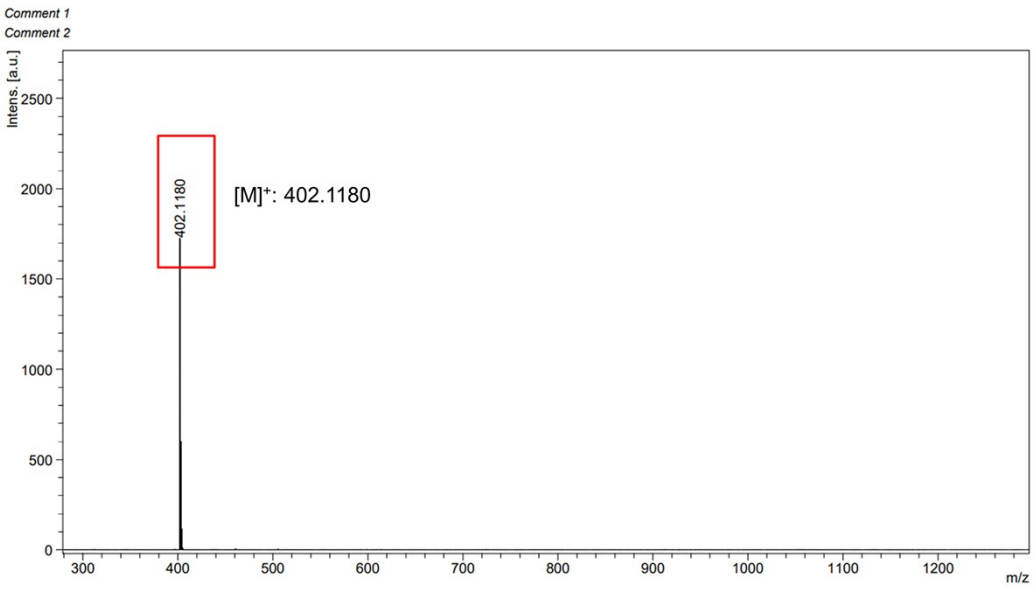


**Fig. S22** High resolution mass spectrum of **PBYN** under illumination condition.

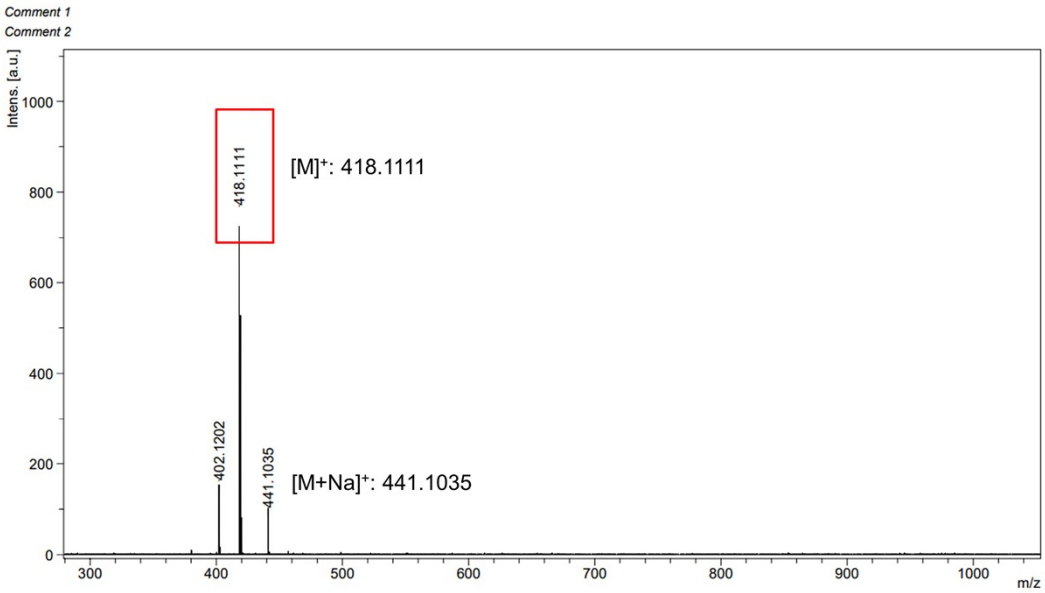



**Fig. S23** High resolution mass spectrum of **OPBYN** under illumination condition.

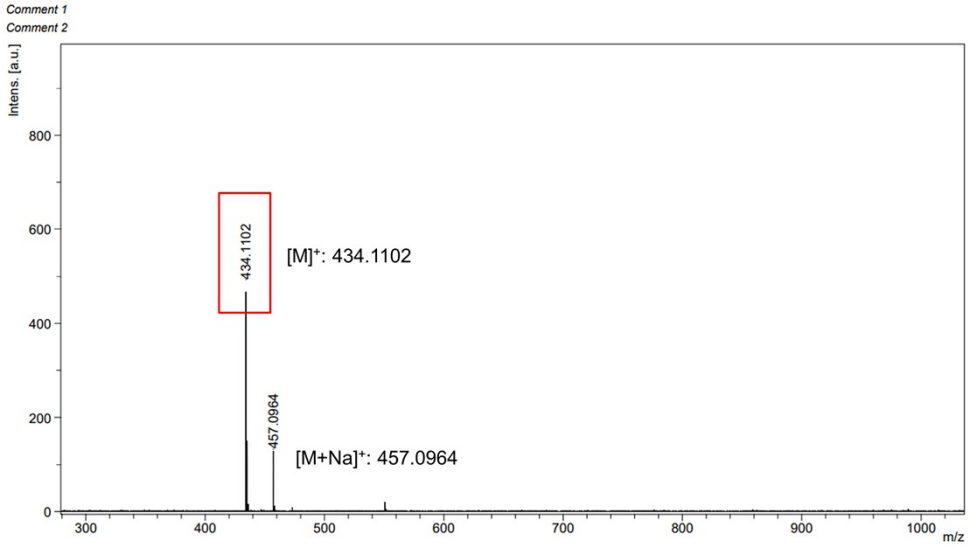



**Fig. S24** High resolution mass spectrum of **DOPBYN** under illumination condition.

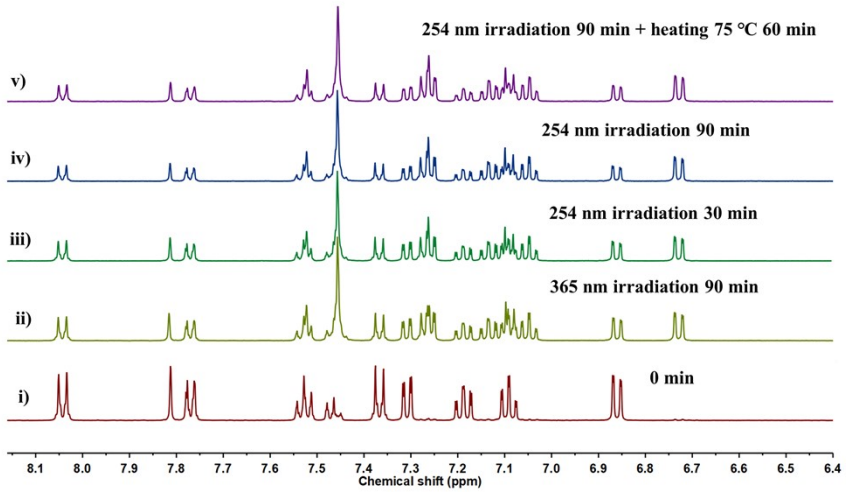



**Fig. S25** $^{1}$H NMR spectra of **PBYN** in $CD_3CN$ solution (3.5 mM) toward different stimuli. i) without light irradiation. ii) 30 min irradiation with a 365 nm light. iii) 30 min irradiation with 254 nm light. iv) 90 min irradiation with 254 nm light. v) heated at 75 °C for 60 min.

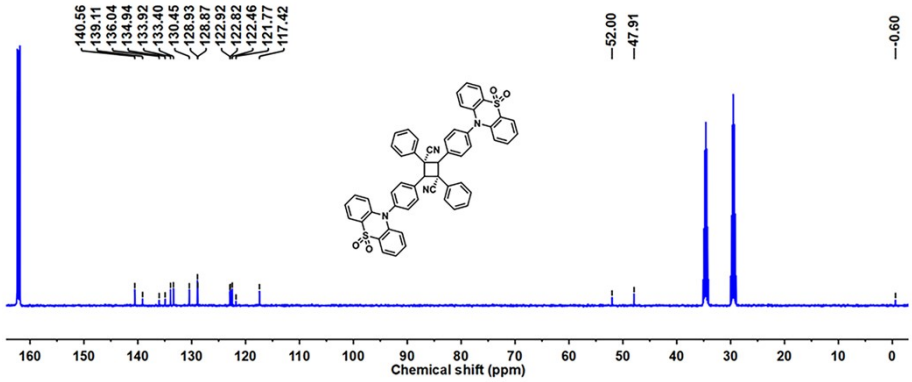



**Fig. S26** $^{13}$C NMR spectrum of **L-DOPBYN** in DMF-$d_7$.

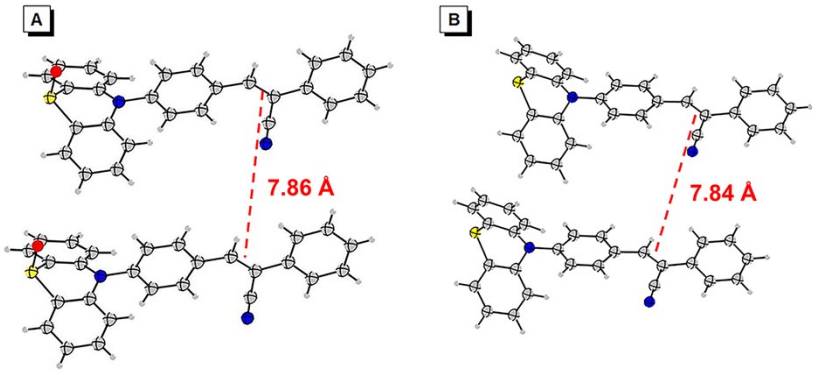
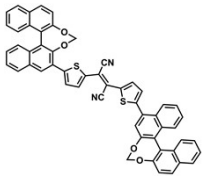
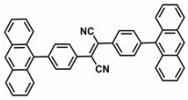
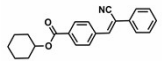
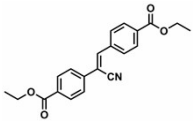
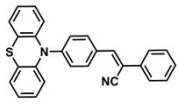
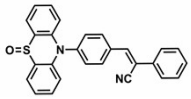
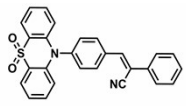



**Fig. S27** The molecular packing of (A) **OPBYN**, (B) **PBYN**

**Table S4** Comparison with the reported analogues.

| Compound | *Z*/*E* Isomerization | Photodimerization |
|---|---|---|
|  **4**[1] | √ | × |
|  **ANTCN**[2] | √ | × |
|  **CSHe**[3] | × | √ |
|  **CSEt**[4] | × | √ |
|  **PBYN** | √ | × |
|  **OPBYN** | √ | × |
|  **DOPBYN** | √ | √ |

## Reference


1. J. Li, H. K. Bisoyi, S. Lin, J. Guo and Q. Li, *Angew. Chem. Int. Ed.*, 2019, **58**, 16052-16056.
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4. P. Li, J. Wang, P. Li, L. Lai and M. Yin, *Mater. Chem. Front.*, 2021, **5**, 1355-1363.