

Supporting Information

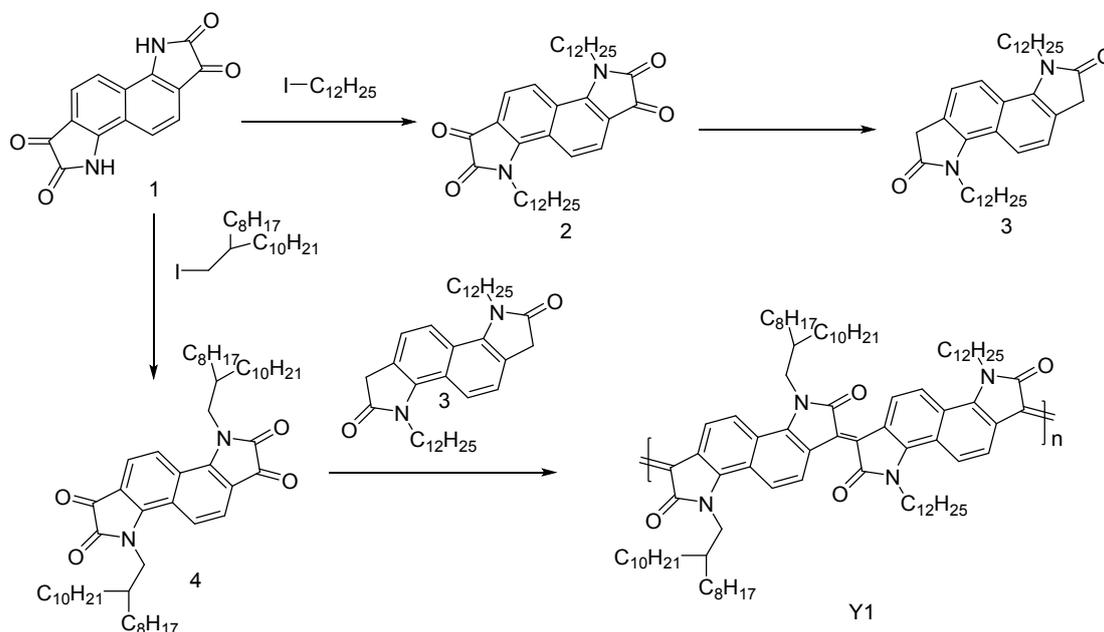
Coupling Molecular Rigidity and Flexibility on Fused Backbones for NIR-II Photothermal Conversion

Content

1. Synthetic Procedures.....	S2
2. General Characterizations.....	S8
3. Calculation of photothermal conversion efficiency.....	S8
4. Data and Explanations.....	S8
5. References.....	S27

1、Synthetic Procedures

Scheme S1: The synthetic route to the Y1.



Compound 1 was synthesized according to literature and used without further purification.^{s1} 1-iodododecane was purchased from the aladdin company, and 9-(iodomethyl)nonadecane was synthesized according to the literature.^{s2}

Compound 2

In an oven dried Schlenk flask, crude bisatin (compound 1) (1.0 g, 3.7 mmol) and dried K₂CO₃ (2.07 g, 15 mmol) were dissolved in dry DMF (15 mL) under argon protection. After the mixture was heated to 60 °C and continuously stirred for 10 minutes, then the 1-iodododecane (3.2 g, 13 mmol) was injected into the reaction. The reaction was heated to 88 °C and stirred overnight. After removing the solvent by evaporator, the crude product was purified by column chromatography on silica gel (eluent: DCM: hexane = 1:1.5) and concentrated in vacuo to yield a blue solid (400 mg, 17.6 % yield). ¹H NMR (400 MHz, CDCl₃, 300K): δ (ppm) = 7.95 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 4.26-4.20 (m, 4H), 1.86-1.77 (m, 2H), 1.50-1.20 (m, 36H), 0.90-0.87 (m, 6H). ¹³C NMR (400 MHz, CDCl₃, 300K): δ (ppm) = 184.15, 160.40,

153.58, 128.65, 121.59, 120.98, 117.60, 44.89, 33.19, 30.79, 30.67, 30.59, 30.50, 28.01, 23.99, 15.42. MS(ESI⁺): C₃₈H₅₄N₂O₄, calculated: 602.40, M+H⁺ found: 603.41.

Compound 3

Compound 2 (320 mg, 0.53 mmol) was suspended in 4.0 mL DMSO with hydrazine hydrate (2.0 mL) and the mixture was heated to 130 °C for 24 hours. The reaction mixture was cooled down, the aqueous phase was then extracted with DCM three times. The combined organic phase was washed with brine, dried with MgSO₄, filtered and then the solvent was removed under reduced pressure. The dark orange crude material was purified by column chromatography on silica gel (eluent: DCM: ethyl acetate = 20:1). The resulting material was concentrated in vacuo to yield a colorless solid (162 mg, 55% yield). ¹H NMR (400 MHz, CDCl₃, 300K): δ = 7.93 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.24 (d, *J* = 7.3 Hz, 4H), 3.67 (s, 4H), 1.86-1.77 (m, 2H), 1.50-1.20 (m, 48H), 0.87 (m, 7H). ¹³C NMR (400 MHz, CDCl₃, 300K): δ = 177.85, 141.98, 123.27, 123.16, 121.64, 117.06, 44.20, 37.40, 33.23, 30.60, 30.86, 30.75, 30.63, 28.14, 24.01, 15.44. MS(ESI⁺): C₃₈H₅₈N₂O₂, calculated: 574.44, M+H⁺ found: 575.45.

Compound 4

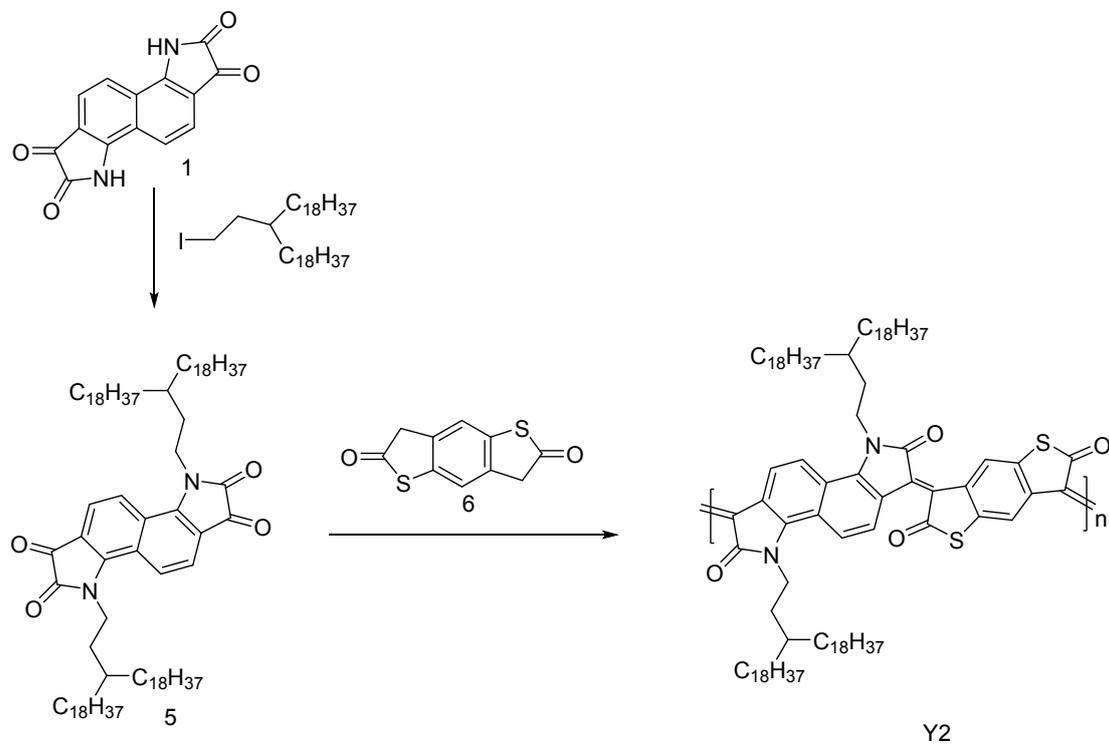
In an oven dried Schlenk flask, crude bisisatin (compound 1) (1.0 g, 3.7 mmol) and dried K₂CO₃ (2.07 g, 15 mmol) were dissolved in dry DMF (15mL) under argon protection. After the reaction mixture was heated to 60 °C and stirred for 10 minutes, then the 1-iodo-2-octyldodecane (6.13 g, 14.8 mmol) was stepwise added into the reaction. The reaction was then heated to 88 °C and stirred overnight. After removing the solvent by evaporator, the crude product was purified by column chromatography on silica gel (eluent: DCM: hexane = 1:1.5) and concentrated in vacuo to yield a blue solid (388 mg, 12.5 % yield). ¹H NMR (400 MHz, CDCl₃, 300K): δ (ppm) = 8.01 (d, *J*

= 8.7 Hz, 2H), 7.68 (d, J = 8.7 Hz, 2H), 4.19-4.17 (m, 4H), 1.87-2.01 (m, 2H), 1.37-1.24 (m, 64H), 0.90-0.87 (m, 12H). ^{13}C NMR (101 MHz, CDCl_3 , 300K): δ (ppm) = 182.70, 159.30, 152.39, 127.42, 120.08, 119.94, 116.35, 47.62, 31.09, 29.95, 29.59, 29.52, 26.20, 22.67, 22.65, 14.10. MS (ESI+): $\text{C}_{54}\text{H}_{86}\text{N}_2\text{O}_4$, calculated: 826.66, $\text{M}+\text{H}^+$ found: 827.38.

Polymer Y1

Compound **3** (95.89 mg, 0.1668 mmol), **4** (138 mg, 0.1668 mmol) and PTSA monohydrate (6.0 mg, 0.2 eq) were placed into a dry 15 mL microwave vial which was capped and evacuated with argon. 6.0 mL of degassed dry toluene was added and the mixture was heated at 110 °C for 5 hours to give a purple solid. Successive soxhlet extractions with methanol, acetone, hexane, CHCl_3 and chlorobenzene. The chlorobenzene gave a single major polymer fraction, which was reduced to minimum volume and precipitated into methanol to give 210 mg of a dark purple solid (92 % yield). GPC (chlorobenzene, 80 °C): M_n = 67.3 KDa, M_w = 266.3 KDa, PDI = 3.95. ^1H NMR (400 MHz, 393 K, 1,1,2,2-tetrachloroethane- d_2) δ (ppm)=: 9.20 – 8.70 (broad), 8.15–7.05 (m), 4.60–3.85 (m), 2.20-0.60 (m).

Scheme S2: The synthetic route to the Y2.



Compound 6 was synthesized according to literature.^{s3}

19-(2-iodoethyl) heptatriacontane was synthesized from the starting material 2-octyldodecan-1-ol,^{s2} which is available from the Desi photoelectric company.

Compound 5

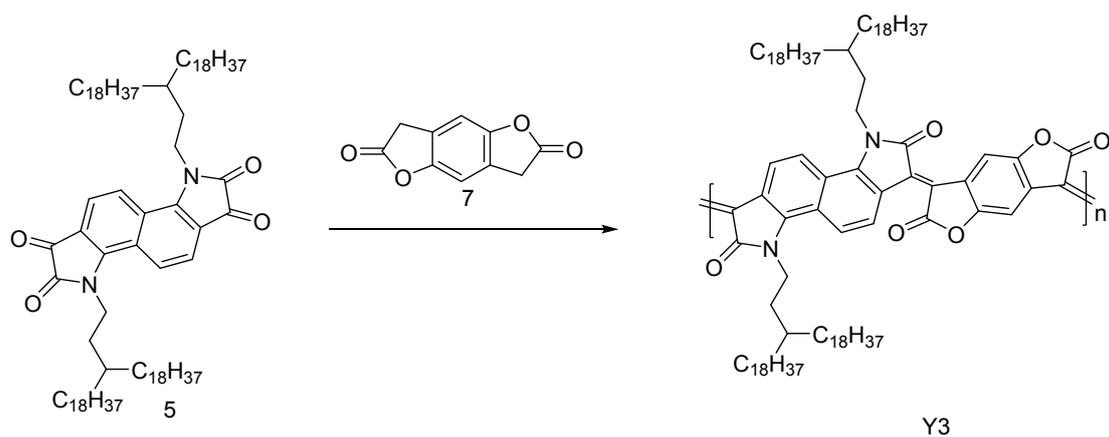
In an oven dried Schlenk flask, crude bis-isatin (compound 1) (1.0 g, 3.7 mmol) and dried K₂CO₃ (2.07 g, 15 mmol) were dissolved in dry DMF (15.0 mL) under argon. After the reaction mixture was heated to 60°C and stirred for 10 minutes, then the 1-iodine-3-octadecylhexane (7.6 g, 11.2 mmol) was injected into the reaction. The reaction was heated to 100 °C and stirred overnight. After removing the solvent by evaporator, the crude product was purified by column chromatography on silica gel (eluent: DCM: hexane = 1:1) and concentrated in vacuo to yield a blue solid (420 mg,

8.2 % yield). ^1H NMR (400 MHz, CDCl_3 , 300K): δ = 7.99 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 4.30-4.21 (m, 4H), 1.81-1.71 (m, 4H), 1.55-1.05 (m, 136H), 0.94-0.86 (m, 12H). ^{13}C NMR (400 MHz, CDCl_3 , 300K): δ = 182.78, 158.98, 152.26, 127.23, 120.09, 119.66, 116.28, 42.13, 35.91, 33.46, 33.17, 31.94, 29.99, 29.72, 29.38, 26.64, 22.70, 14.12. MS(ESI+): $\text{C}_{92}\text{H}_{162}\text{N}_2\text{O}_4$, calculated:1359.2535, $\text{M}+\text{H}^+$ found: 1360.2547.

Polymer Y2

To a vial was added compound **5** (80.95 mg, 0.0595 mmol, 1equiv) and compound **7** (24.39 mg, 0.04 mmol, 1equiv), PTSA (2.0 mg). The tube was sealed and flushed with Argon, and then 0.7 mL degassed toluene was added. The mixture was thoroughly degassed under Argon for half an hour, and then the argon inlet was removed. The vial was heated at 120 °C for 3 days. After cooling to room temperature, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane and chloroform. The chloroform fractions were concentrated and precipitated into methanol. The precipitates were filtered and dried under vacuum to afford **Y2** as a dark purple solid (65 mg, 70 %). GPC (chlorobenzene, 80°C): M_n = 21.1 KDa, M_w = 31.2 KDa, PDI = 1.48. $^1\text{HNMR}$ (TCE-d_2 , 403 K, 400Hz): δ = 8.71 (broad), 8.01 (broad), 7.57 (broad), 4.33 (broad), 2.12-0.76 (m).

Scheme S3: The synthetic route to the Y3.



Compound 7 was synthesized according to literature.^{s4}

Polymer Y3

A vial was added compound **5** (71.82 mg, 0.053 mmol, 1 equiv) and compound **6** (10.04 mg, 0.053 mmol, 1 equiv), PTSA (2.0 mg). The tube was sealed and flushed with Argon, and then 0.5 mL degassed toluene was added. The mixture was thoroughly degassed under Argon for half an hour, and then the argon inlet was removed. The vial was heated at 120 °C for 3 days. After cooling to room temperature, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane and chloroform. The chloroform fraction was concentrated and precipitated into methanol. The precipitates were filtered and dried under vacuum to afford **Y3** as a black solid (59 mg, 73 %). GPC (chlorobenzene, 80°C): Mn= 25.2 KDa, Mw= 44.3 KDa, PDI= 1.76. ¹HNMR (TCE-d₂,

403 K, 400Hz): $\delta = 9.04$ (broad), 7.76 (broad), 4.34 (broad), 2.18-0.85 (m).

2、 General Characterizations

Absorption spectra of all the polymer solutions were recorded on SHIMADZU UV-3600 spectrometer with temperature-control attachment. The fluorescence spectra were measured on an INNOLAS SpitLight EVO OPO laser source (1064 nm, 11 mJ/100 Hz) and an EDINBURGH INSTRUMENTS FLS 980 detector (1 nm/point, the interval is 0.1s, 1100-1800nm). Thermal gravity analyses (TGA) were carried out on a Thermogravimetric Analyzer from Nicolet 6700 at a rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was performed on a DSC8000 (PerkinElmer) apparatus. The thermal infrared images were obtained from a Fluke Tix 660 camera. All optical images were captured by a Canon EOS 70D digital camera. The molecules were optimized at the PBE1PBE/6-311G* level, using the Gaussian 09 software package and Multiwfn.

3、 Calculation of photothermal conversion efficiency

The photothermal conversion efficiency (η) was measured with a cuvette of optical path 1.0 mm. IR camera was used to monitor the temperature change and 1064 laser was used to irradiate the cuvette. η can be calculated according to eq (S1):

$$\eta = \frac{Q}{P} \quad (\text{S1})$$

Where Q is the heat per unit time produced by light irradiation and P is the light power. The key of the equation is the calculation of Q. The heating process could record through equation (3). Since the m and C_p of the solutions and cuvette could be detected

by a balance and DSC, Q can be calculated by fitting the temperature-time curve.

4、 Data and Explanations

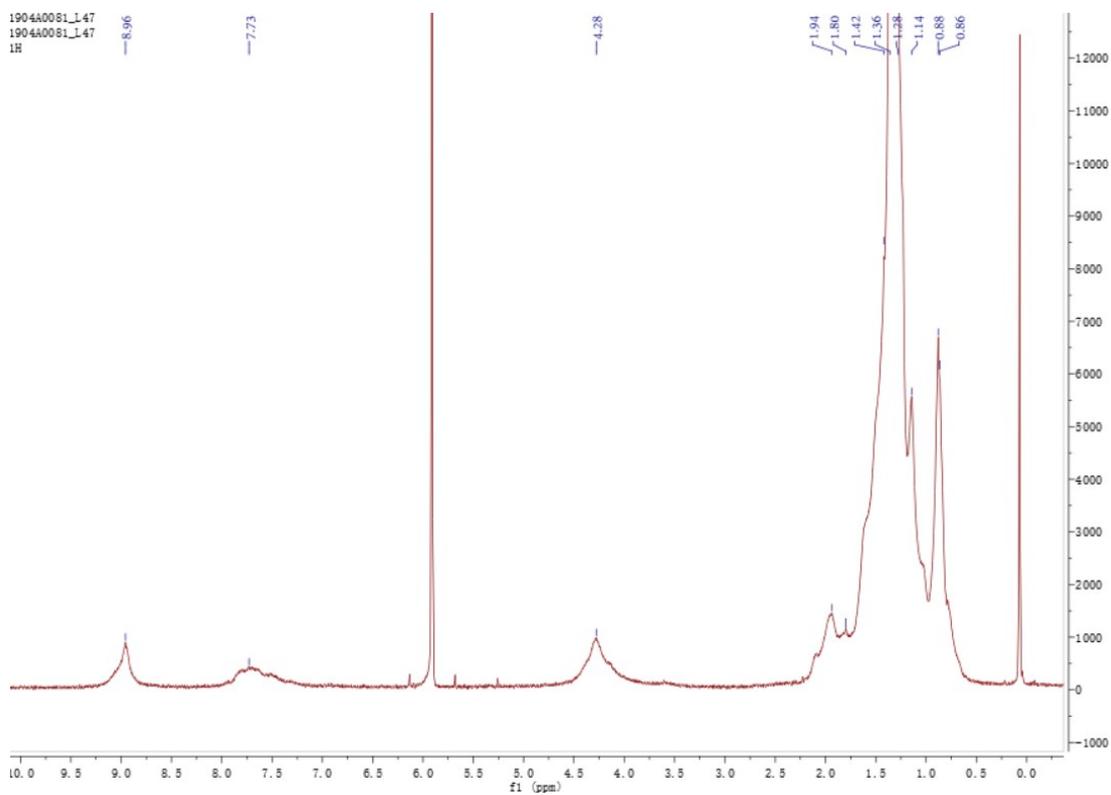


Fig. S1 ^1H NMR spectrum of **Y1** (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 393K).

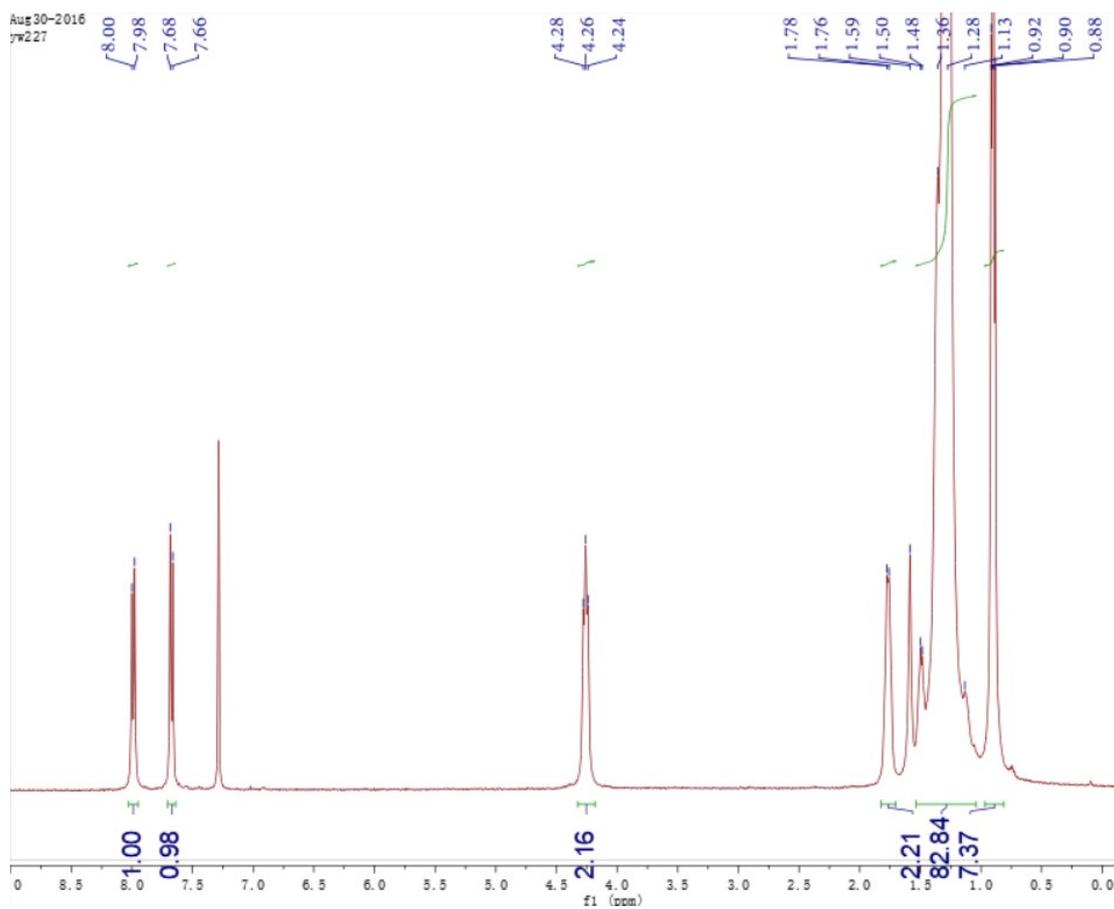


Fig. S2 ^1H NMR spectrum of compound **5** (CDCl_3 , 400 MHz, 300 K)

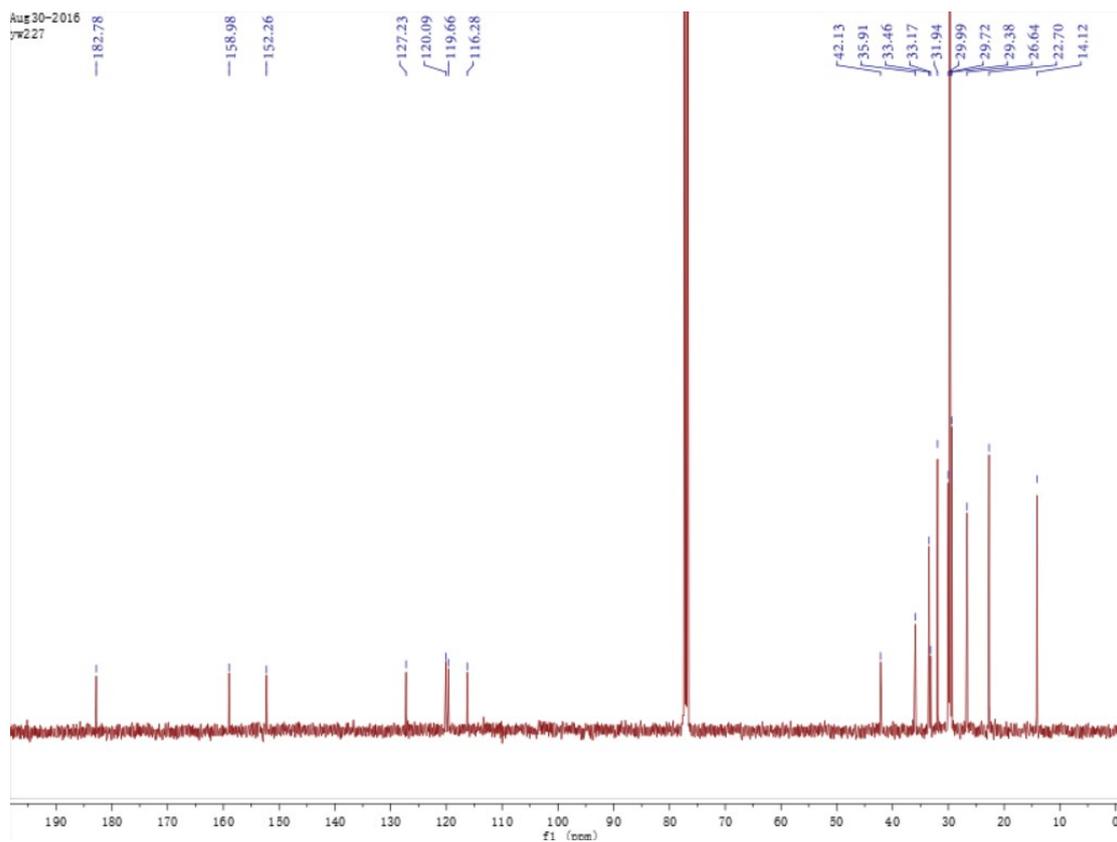


Fig. S3 ^{13}C NMR spectrum of compound **5** (CDCl_3 , 400 MHz, 300 K).

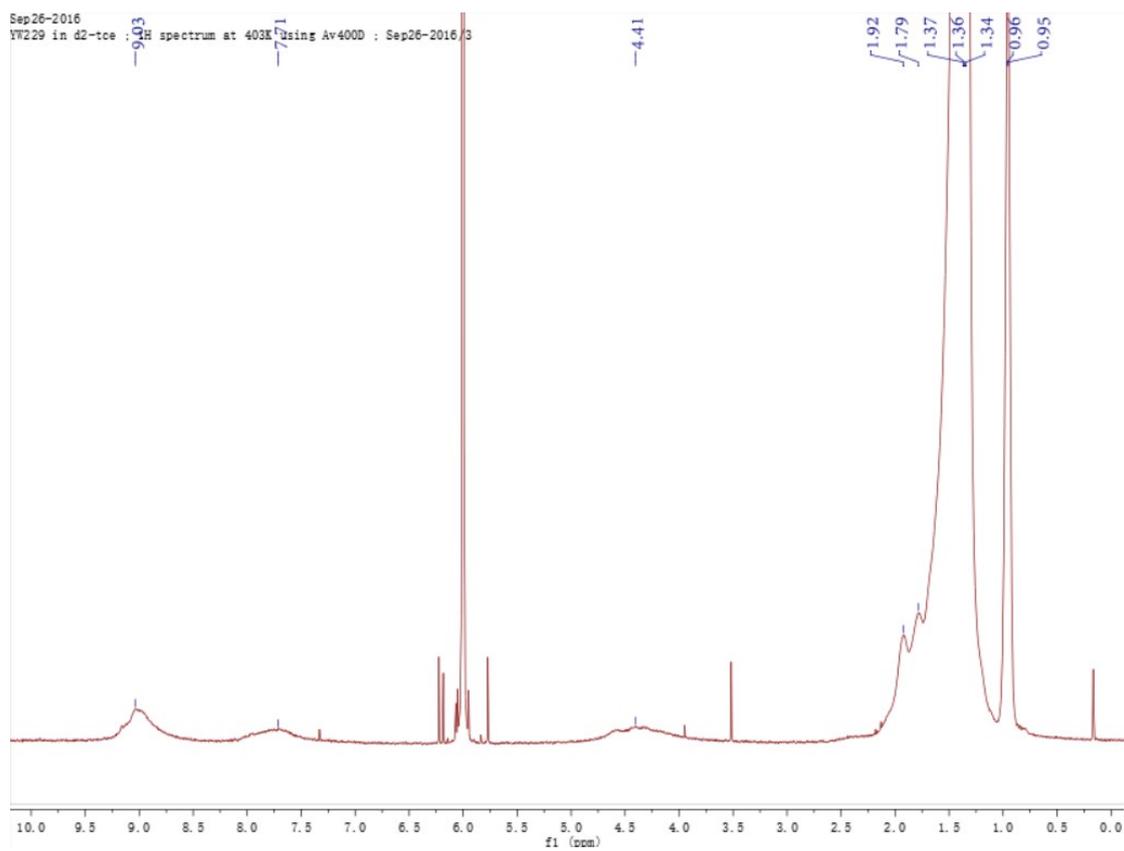


Fig. S5 ¹H NMR spectrum of **Y3** (1,1,2,2-tetrachloroethane-d₂, 400 MHz, 403K).

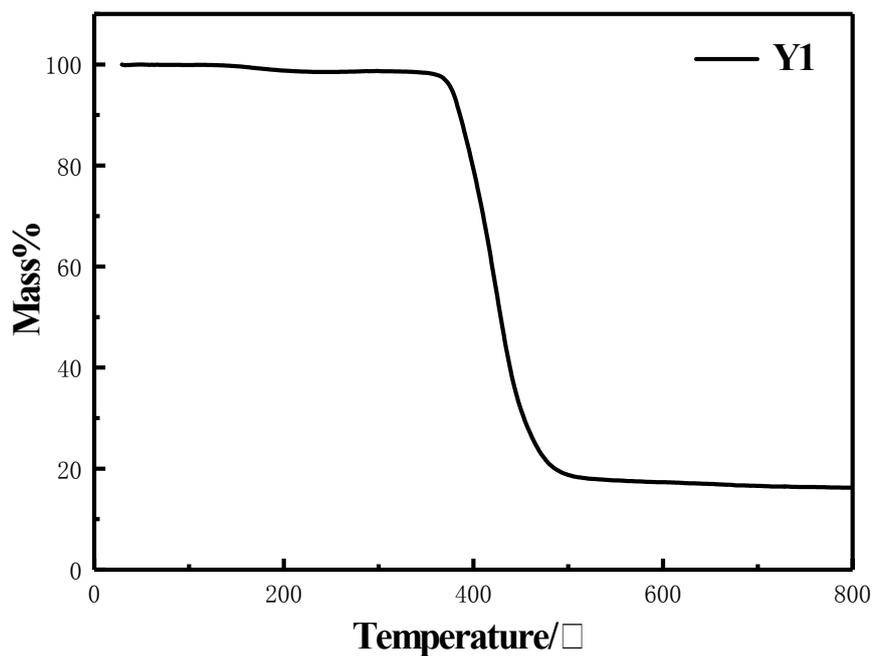


Fig. S6 Thermogravimetric analysis (TGA) of polymer Y1, with 5 % decomposition temperature at 377°C.

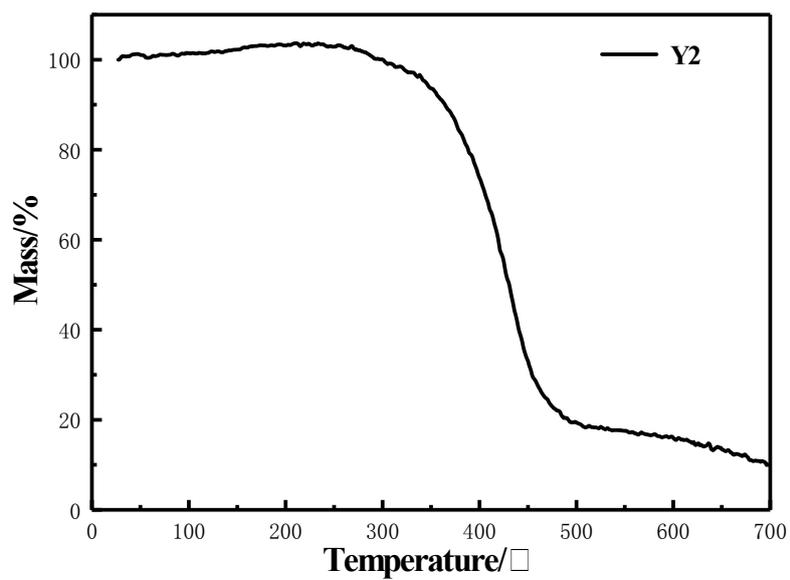


Fig. S7 Thermogravimetric analysis (TGA) of polymer Y2, with 5 % decomposition

temperature at 345°C.

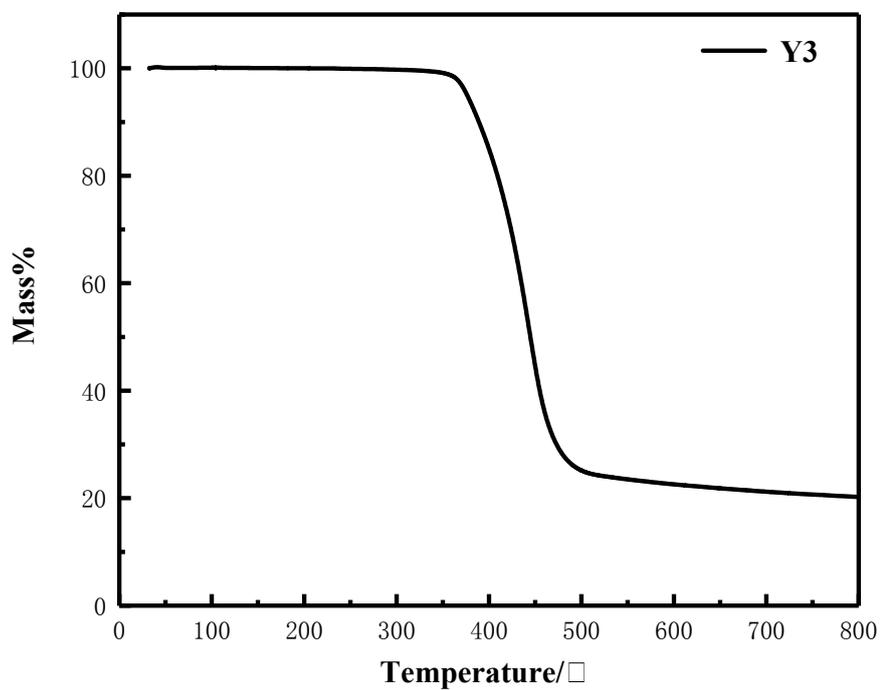


Fig. S8 Thermogravimetric analysis (TGA) of polymer Y3, with 5 % decomposition temperature at 376°C.



Fig. S9 Images of NIR II photothermal polymer in chlorobenzene. From top to bottom,

the images are assigned to Y1, Y2, and Y3, respectively. The corresponding concentrations of each row are 400 $\mu\text{g/mL}$, 200 $\mu\text{g/mL}$, 100 $\mu\text{g/mL}$, and 50 $\mu\text{g/mL}$ and 25 $\mu\text{g/mL}$, from left to right, respectively.

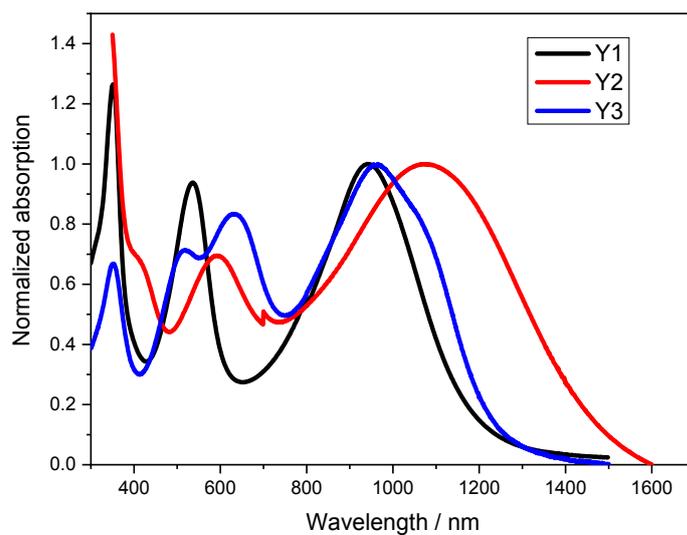


Fig. S10 Normalized thin films absorption spectra of three polymers.

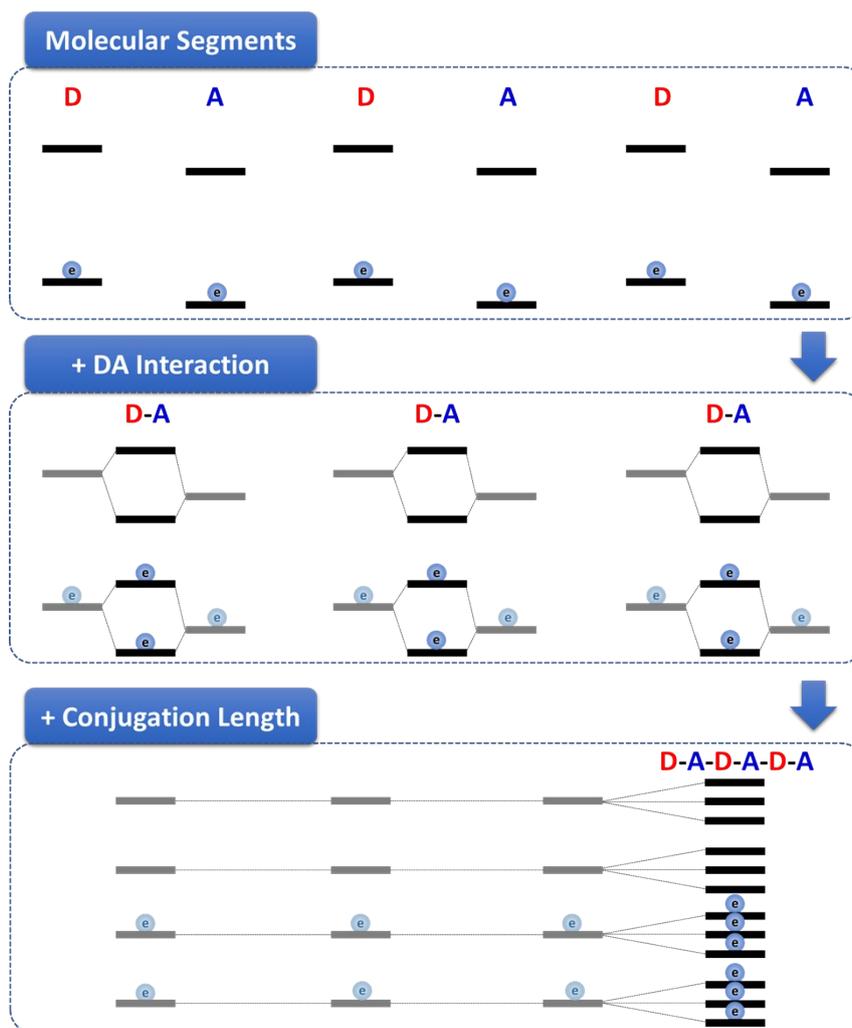


Fig. S11 The schematic illustration of the formation of energy levels of low-gap conjugated polymers, in which the two main factors, DA effect and conjugated length, are taken into consideration separately in order to facilitate understanding. As shown in the Fig., the energy of a single donor fragment (D) is higher than that of a single acceptor fragment (A). When the D is bonded with the A, the orbitals will be reorganized, and the HOMO energy level of the formed D-A fragment is mainly composed of the original donor fragment, but the energy is higher than that of the original donor fragment, while the LUMO energy level is mainly composed of the acceptor fragment, but the energy is lower than the LUMO of the original acceptor fragment. If the LUMO energy of the A is raised, The proportion of the acceptor

segment in the LUMO energy level of the D-A fragment will decrease, for example, when the LUMO of the A is almost the same as that of the D, their contribution to the LUMO energy level of the D-A fragment is almost the same. Finally, the D-A fragments form a larger polymer, and the orbitals continue to split and reassemble, and the corresponding energy gap is further reduced.

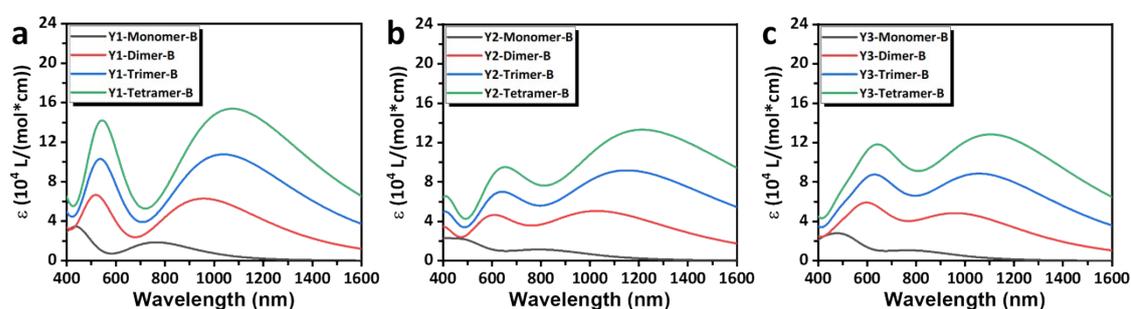


Fig. S12 Simulated absorption spectra of molecules with different degrees of polymerization, the position of the absorption peak and the extinction coefficient correspond to the transition energy and oscillator strength of the above Fig..

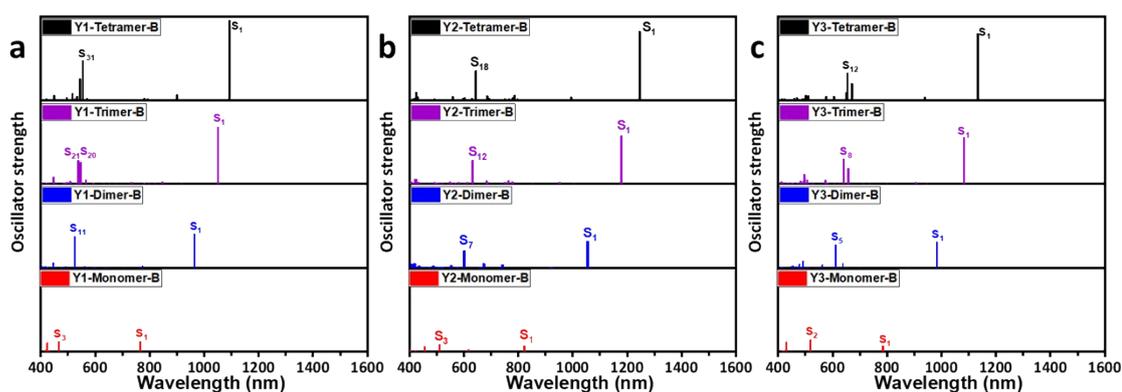


Fig. S13 The corresponding transitions and oscillator strengths of the absorption peaks of molecules with different degrees of polymerization. As shown in the Fig., the main absorption peaks of all molecules correspond to the transition of S_0 - S_1 . In the case of

the same degree of polymerization, the corresponding wavelength of the transition energy is $Y2 > Y3 > Y1$, while the oscillator strength is $Y1 > Y3 > Y2$.

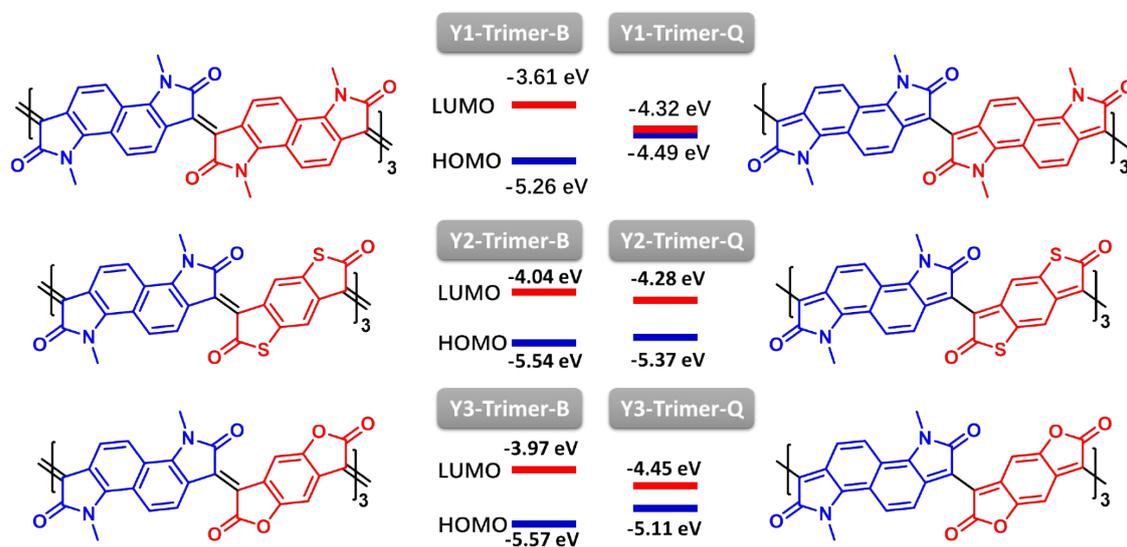


Fig. S14 The aromatic and the quinoid structures of the trimers and the energy level calculated from their optimal conformation.

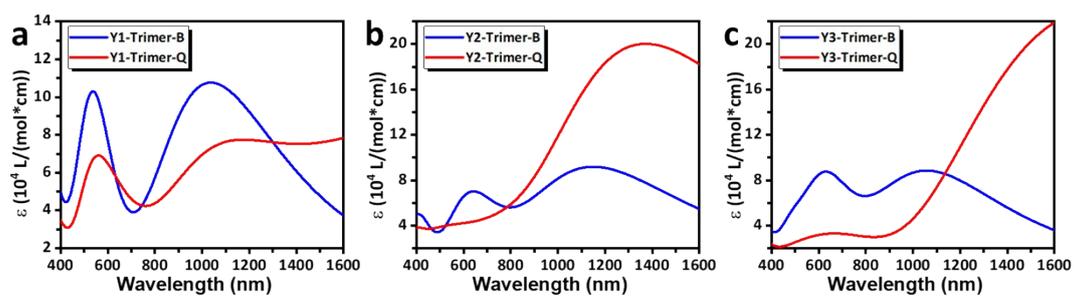


Fig. S15 Absorption spectra calculated from the aromatic and quinoid structures of trimer.

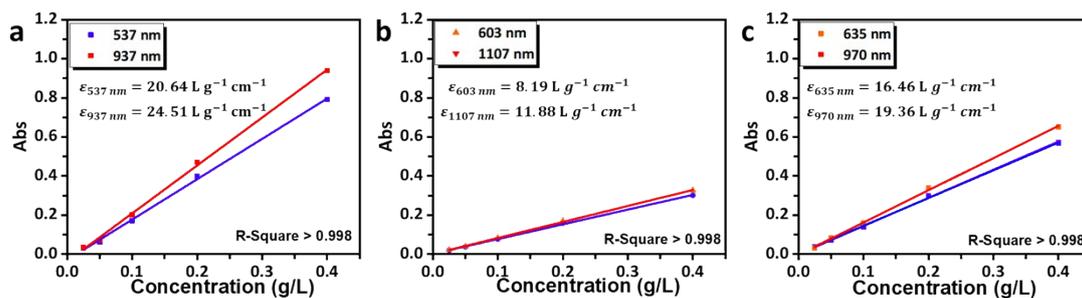


Fig. S16 The absorbance at the main absorption peaks of NIR II photothermal polymers at different concentrations. The R-Squares of all linear fitting is greater than 0.998, and the mass extinction coefficients calculated according to the curves are marked in the Fig.s.

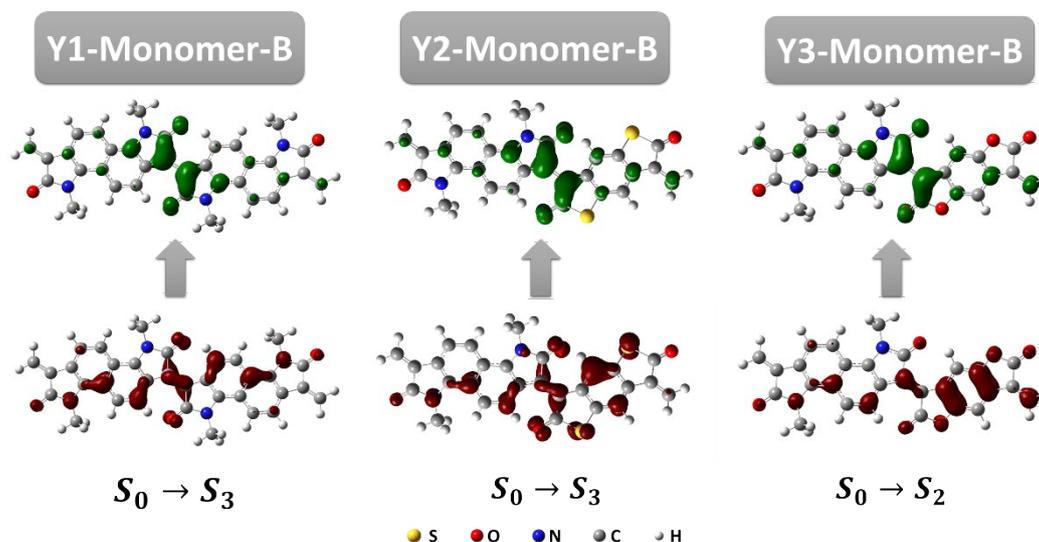


Fig. S17 The electron cloud change of the transition corresponding to the second largest absorption. Some characteristics of DA electron transfer can be observed, especially for Y2 and Y3, in which the electron transfer from the benzene ring to the electron-deficient dipolar carbonyl groups.

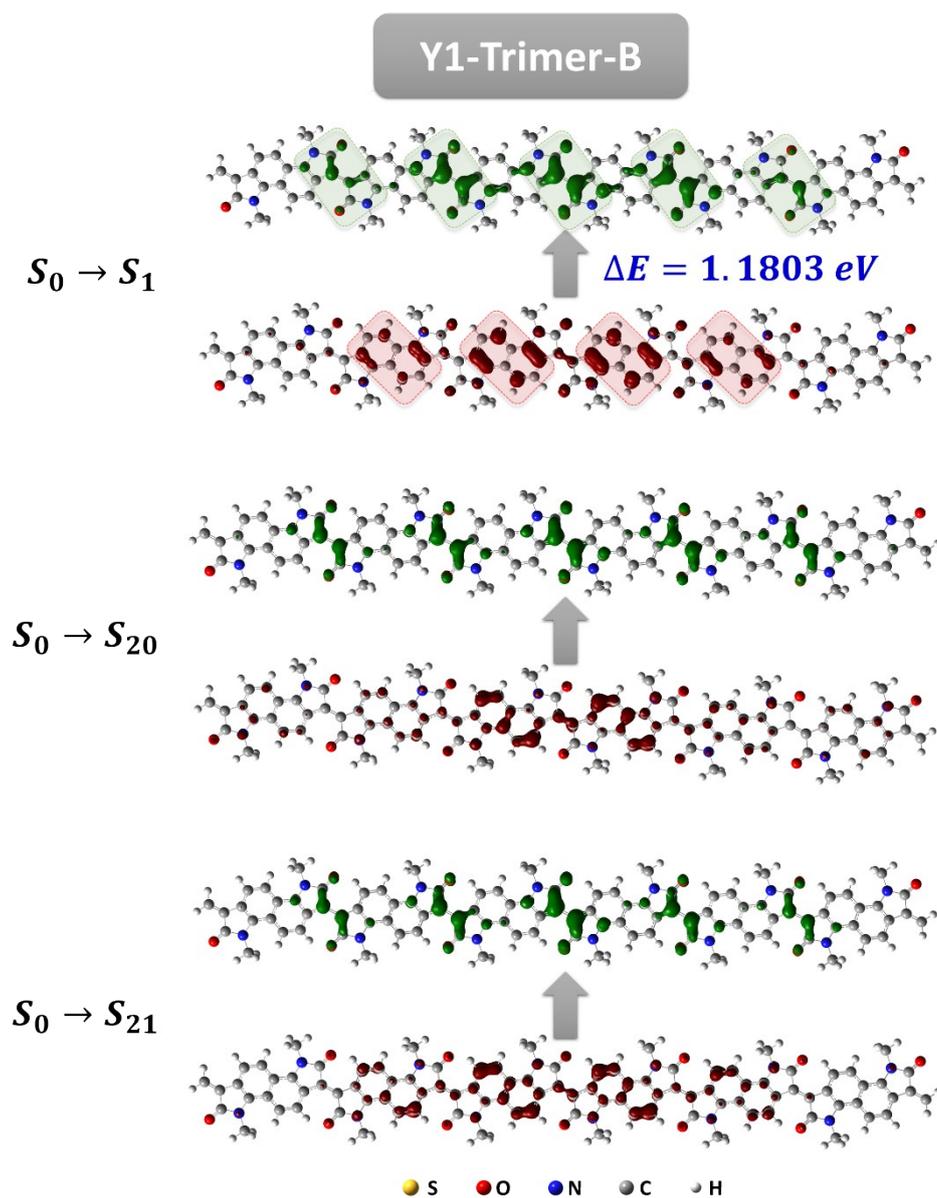


Fig. S18 The electron cloud change of the transition corresponding to the largest and second largest absorption for Y1-Trimer-B.

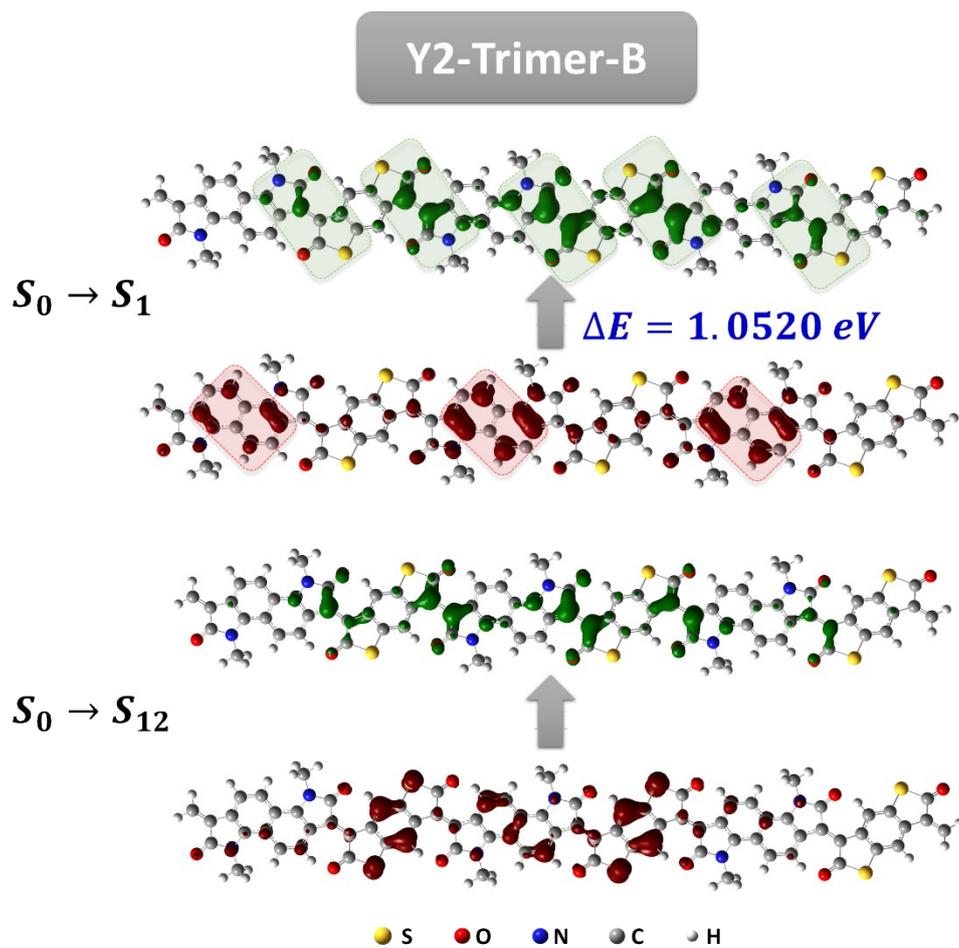


Fig. S19 The electron cloud change of the transition corresponding to the largest and second largest absorption for Y2-Trimer -B.

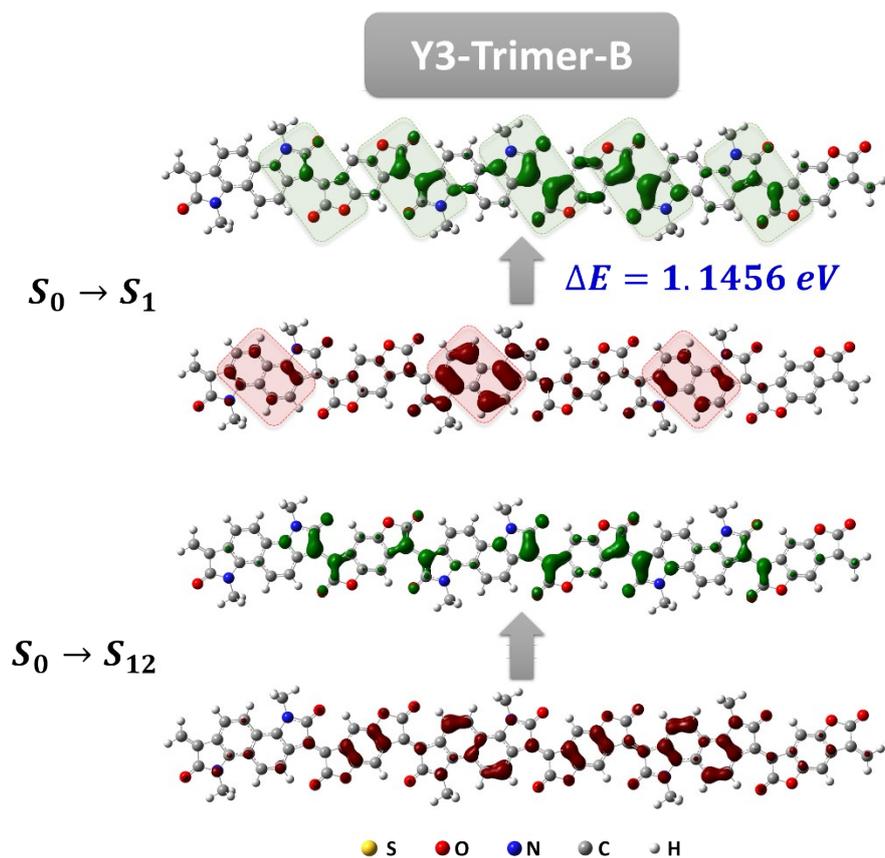


Fig. S20 The electron cloud change of the transition corresponding to the largest and second largest absorption for Y3-Trimer -B.

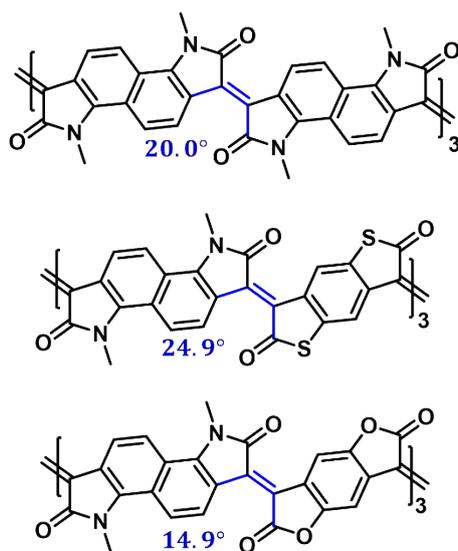


Fig. S21 The dihedral angles of the trimers with optimal configuration at the ground state.

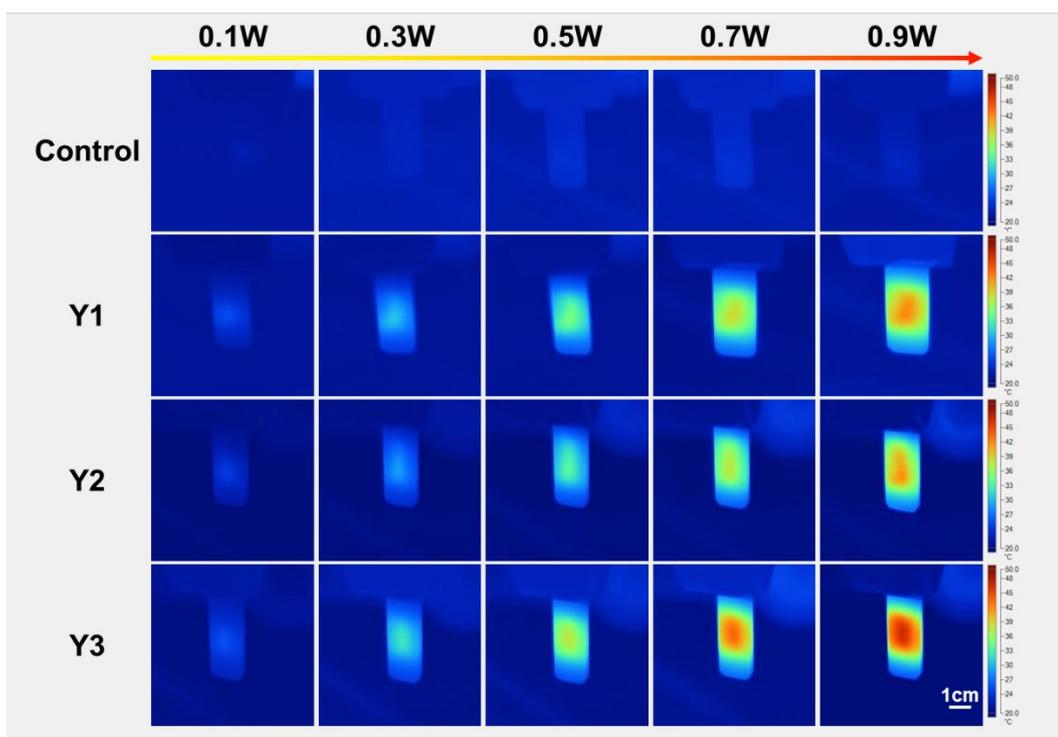


Fig. S22 Temperature distributions of the polymer solution irradiated by laser of different power for 2 minutes.

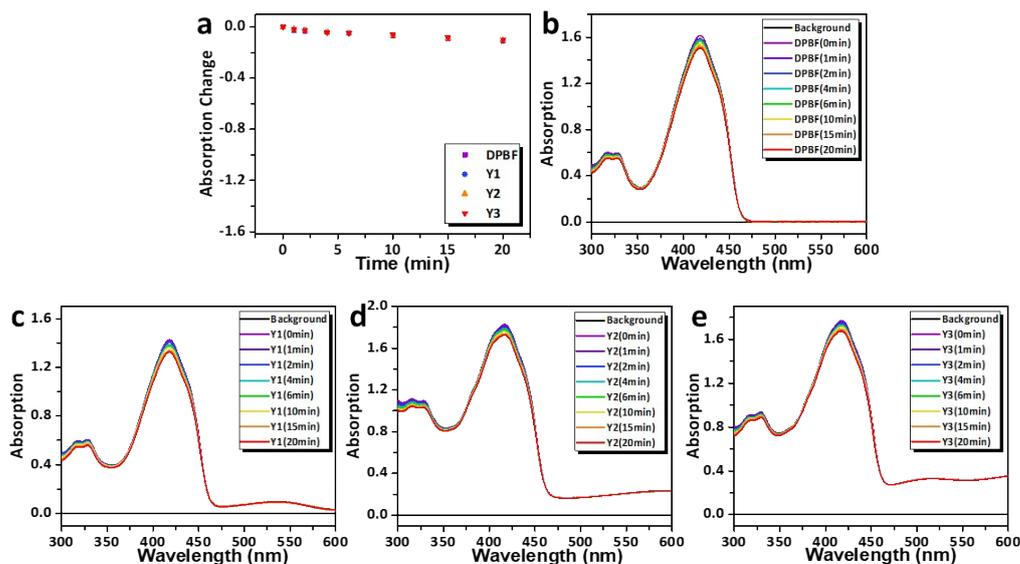


Fig. S23 Detection of singlet oxygen by DPBF. a) absorption change in 418 nm of DPBF, Y1, Y2, and Y3. Their chlorobenzene solutions (30 ug/mL polymers with 1 mg/mL DPBF) have been continuously pumped into oxygen and irradiated with a 1064nm laser (1 W) for different time. The UV absorption spectra are provided in b, c, d, and e. These experiments prove that the ISC process are low-efficient to some extent.

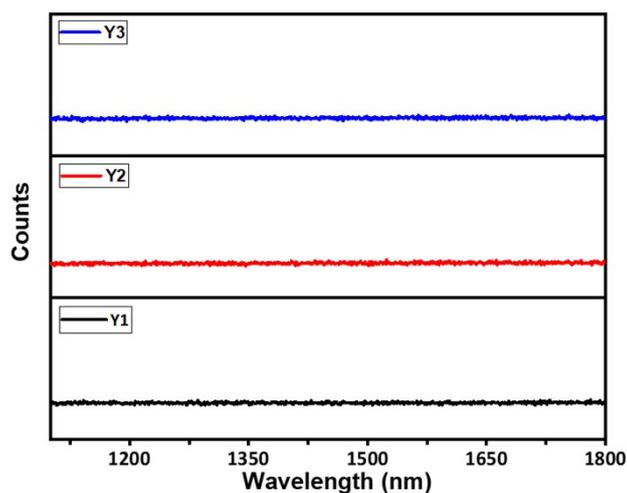


Fig. S24 Fluorescence spectrum of NIR II photothermal polymer. The wavelength of excitation light is 1064 nm, and the intensity is 11 mJ/100Hz. The scanning speed is 1

nm/point with interval of 0.1 s.

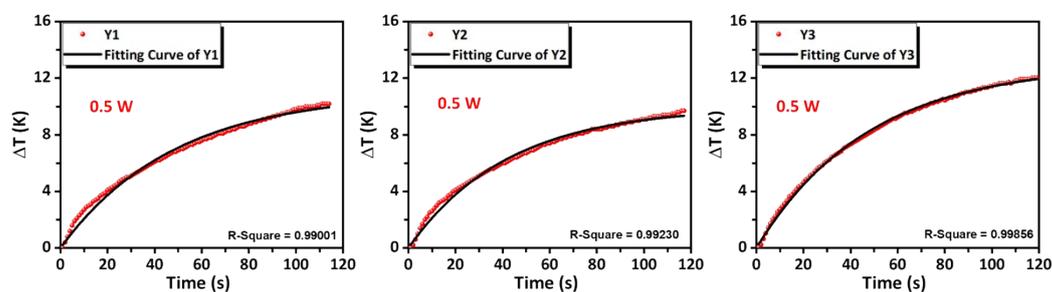


Fig. S25 Temperature changes under the irradiation of 1064 nm and 0.5 W and its fitting curve.

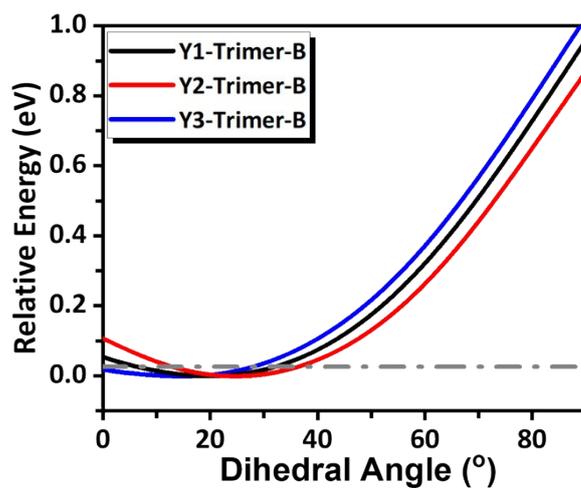


Fig. S26 The energy scan of three trimers with different dihedral angles. The gray dash-dot represents the energy of 300 K, which is 0.026 eV.

Table S1 RESP charges of different atoms in ground states (without apostrophe) and excited states (with apostrophe).

	Y1-Trimer-B	Y2-Trimer-B	Y3-Trimer-B
Q_1	0.0002	-0.1268	-0.3629
Q_1'	-0.0037	-0.1337	-0.3632
Q_2	0.4551	0.4139	0.6958
Q_2'	0.4640	0.4145	0.6938
Q_3	-0.0763	-0.0451	-0.0488
Q_3'	-0.0904	-0.0271	-0.0535
Q_4	-0.0838	-0.1113	-0.1553
Q_4'	-0.0894	-0.1413	-0.1636
Q_5	-0.4805	-0.3869	-0.4975
Q_5'	-0.4805	-0.3900	-0.4980
Q_6	0.1994	0.2066	0.2013
Q_6'	0.2027	0.2077	0.2033

References

- s1 A. Onwubiko, W. Yue, C. Jellet, M. Xiao, H.-Y. Chen, M. K. Ravva, D. A. Hanifi, A.-C. Knall, B. Purushothaman, M. Nikolka, J.-C. Flores, A. Salleo, J.-L. Bredas, H. Sirringhaus, P. Hayoz, I. McCulloch, *Nat. Comm.*, 2018, **9**, 416.
- s2 I. Meager, R. S. Ashraf, S. Mollinger, B. C. Schroeder, H. Bronstein, D. Beatrup, M. S. Vezie, T. Kirchartz, A. Salleo, J. Nelson, and I. McCulloch, *J. Am. Chem. Soc.*, 2013, **135**, 11537-11540.
- s3 Y. He, J. Quinn, Y. Deng, Y. Li, *Org. Electron.*, 2016, **35**, 41-46.
- s4 T. Lei, J.-H. Dou, X.-Y. Cao, J.-Y. Wang, and J. Pei, *J. Am. Chem. Soc.*, 2013, **135**, 12168-12171.