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Ultralow-acceptor-content supramolecular light-harvesting system for white-light emission

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1. Materials, methods, and abbreviations

General

All chemicals, reagents and solvents were purchased from commercial suppliers and used, unless otherwise stated, without further purification. If needed, solvents were dried by literature known procedures. All yields were given as isolated yields. Compound **5**[S1] and **4**[S2] were synthesized according to literatures.

NMR spectroscopy

The ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AVANCE III (300 MHz) spectrometer and calibrated against the residual proton signal or natural abundance carbon resonance of the used deuterated solvent from tetramethylsilane (TMS) as the internal standard. The chemical shifts δ are indicated in ppm and the coupling constants J in Hz. The multiplicities are given as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), and m (multiplet).

Mass spectrometry

High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent Technologies 6540 UHD Accurate-Mass. High performance liquid chromatography (HPLC) analysis was performed on Agilent 1260 HPLC.

Transmission electron microscope (TEM)

TEM investigations were carried out on a JEM-2100 instrument.

Dynamic light scattering (DLS)

DLS measurements were carried out on a Brookhaven BI-9000AT system, equipped with a 200 mW polarized laser source ($\lambda = 514$ nm) at a scattering angle of 90°. All samples were prepared according to the corresponding procedures mentioned above.

UV-Vis spectroscopy

The UV-Vis absorption spectra were measured on a Perkin Elmer Lambda 35 UV-Vis Spectrometer.

Fluorescence spectroscopy

Fluorescence measurements were performed on an Agilent Cary Eclipse spectrofluorometer.

Fluorescence lifetimes

The fluorescence lifetimes were measured employing time correlated single photon counting on a FLS980 instrument with a pulsed xenon lamp. Analysis of fluorescence decay curves were subjected to fit a mono-exponential or bi-exponential decay.

Quantum yields

The quantum yields were carried out on a FLS980 instrument with the integrating sphere.

CIE coordinates

The CIE (Commission Internationale de l'Eclairage) 1931 coordinates were calculated with the method of color matching functions.

Viscometry

Viscosity measurements were carried out with Ubbelohde micro viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 298 K in chloroform and acetonitrile.

Abbreviations

UPy = 2-ureido-4[1H]-pyrimidinone; NPs = nanoparticles; DCM = dichloromethane

$CHCl_3$ = trichloromethane; M = mol/L; br = broad; Ar = aromatic group

2. Fluorescence lifetime measurements

Table S1. Fluorescence lifetimes of **DBT@CSU** NPs (D:A = 100/1) upon excitation at 365 nm in aqueous solution, [**CSU**] = 5×10^{-5} M, [**DBT**] = 5×10^{-7} M, respectively.

Sample	τ_1/ns	RW1[%]	τ_2/ns	RW2[%]	τ/ns	χ^2
CSU	0.43	15.6	3.17	84.4	2.74	1.155
DBT@CSU (**CSU** : **DBT** = 100 : 1)	0.27	50.4	2.77	49.6	1.51	1.111

3. Quantum yield measurements

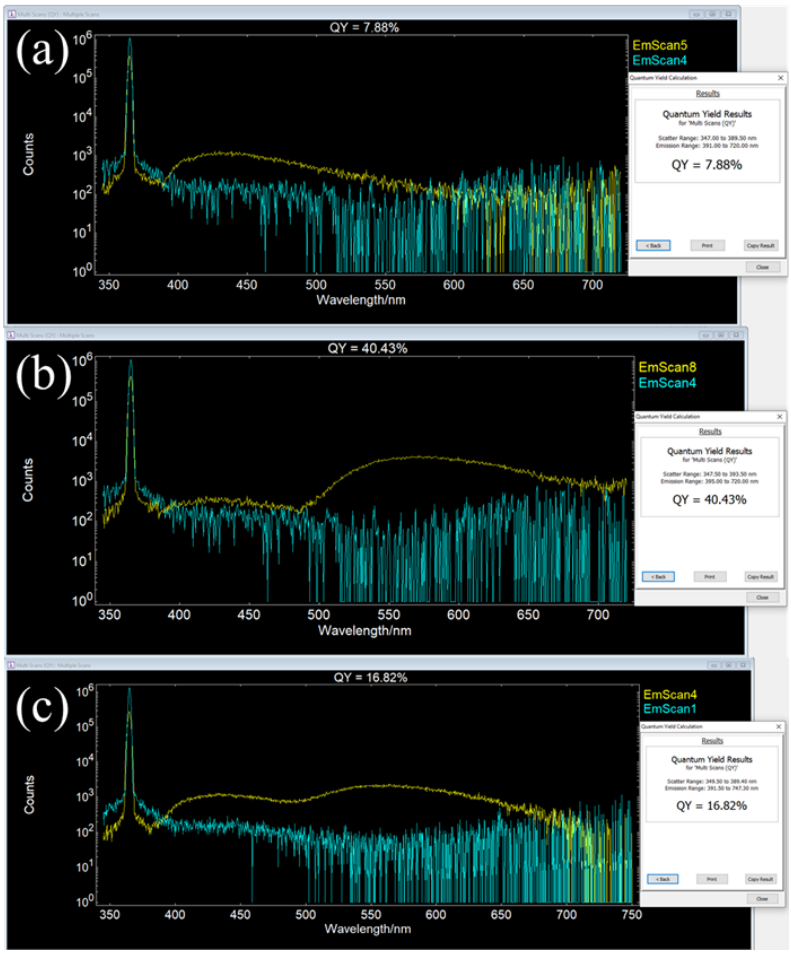


Fig. S1 Absolute fluorescence quantum yields ($\Phi_{f(abs)}$) of (a) NPs of **CSU**, (b) NPs of **DBT@CSU** (**CSU**/**DBT** = 100/1), (c) NPs of **DBT@CSU** (**CSU**/**DBT** = 1000/1), upon excitation at 365 nm in aqueous solution. [**CSU**] = 5×10^{-5} M.

Table S2. Fluorescence quantum yields of NPs of **CSU, DBT@CSU** and white light emission coordinate. [**CSU**] = 5 × 10^{-5} M.

Sample	Fluorescence quantum yields ($\Phi_{f(abs)}$)
CSU	7.88%
DBT@CSU (**CSU : DBT** = 100 : 1)	40.43%
DBT@CSU (**CSU : DBT** = 1000 : 1)	16.82%

4. Energy-transfer efficiency calculation

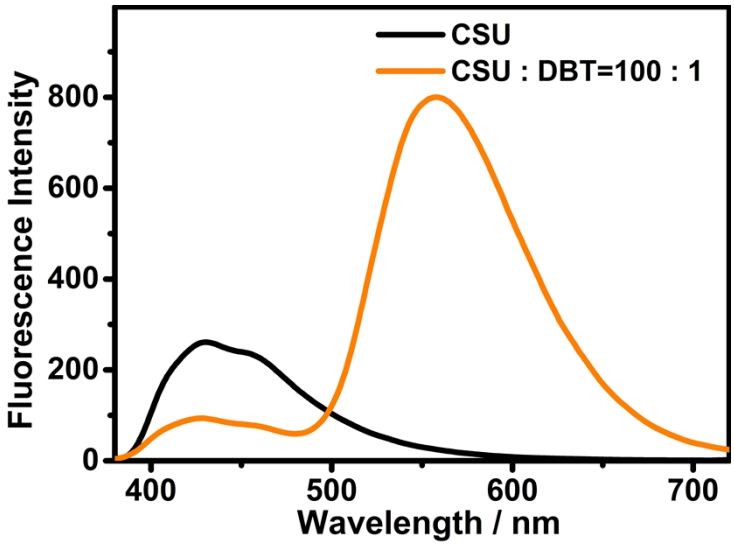


Fig. S2 Fluorescence spectra of **CSU** and **DBT@CSU**, [**CSU**] = 5 × 10^{-5} M, [**DBT**] = 5 × 10^{-7} M, respectively.

Energy-transfer efficiency (Φ_{ET}) was calculated from fluorescence spectra through the equation S1[S3]:

$$\Phi_{ET} = 1 - I_{DA} / I_D \quad \text{(eq. S1)}$$

Where I_{DA} and I_D are the fluorescence intensities of NPs of **DBT@ CSU** (donor and acceptor) and NPs of **CSU** (donor) at 430 nm when excited at 365 nm, respectively.

The energy-transfer efficiency (Φ_{ET}) was calculated as 64.3% in water, measured under the condition of **[CSU]** = 5 × 10^{-5} M, [**DBT**] = 5 × 10^{-7} M, and λ_{ex} = 365 nm.

Table S3. Energy-transfer efficiency with different D/A ratio.

Sample	Concentration, respectively	Energy-transfer efficiency (Φ_{ET})
DBT@CSU (**CSU : DBT** = 100 : 1)	**[CSU]** = 5×10^{-5} M [**DBT**] = 5×10^{-7} M	64.3%
DBT@CSU (**CSU : DBT** = 150 : 1)	**[CSU]** = 5×10^{-5} M [**DBT**] = 3.33×10^{-7} M	58.7%
DBT@CSU (**CSU : DBT** = 200 : 1)	**[CSU]** = 5×10^{-5} M [**DBT**] = 2.5×10^{-7} M	56.7%
DBT@CSU (**CSU : DBT** = 300 : 1)	**[CSU]** = 5×10^{-5} M [**DBT**] = 1.67×10^{-7} M	52.3%
DBT@CSU (**CSU : DBT** = 500 : 1)	**[CSU]** = 5×10^{-5} M [**DBT**] = 1×10^{-7} M	41.8%
DBT@CSU (**CSU : DBT** = 750 : 1)	**[CSU]** = 5×10^{-5} M [**DBT**] = 6.67×10^{-8} M	37.8%
DBT@CSU (**CSU : DBT** = 1000 : 1)	[**CSU**] = 5×10^{-5} M [**DBT**] = 5×10^{-8} M	23.3%
DBT@CSU (**CSU : DBT** = 1500 : 1)	[**CSU**] = 5×10^{-5} M [**DBT**] = 3.33×10^{-8} M	12.2%

5. Antenna effect calculation

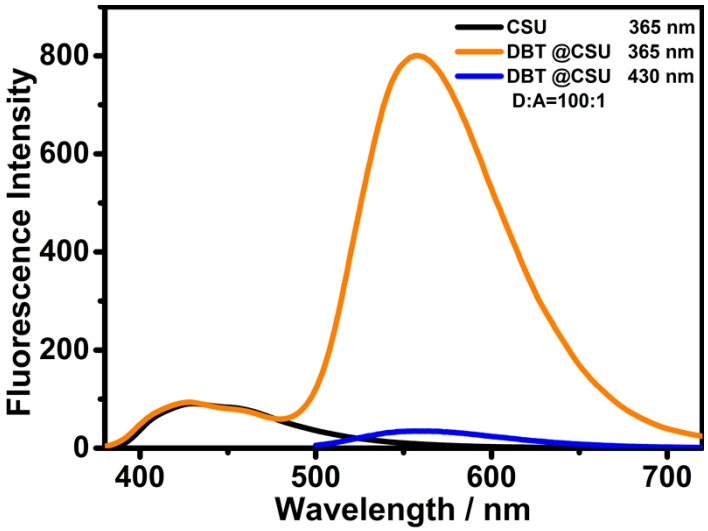


Fig. S3 Fluorescence spectra of **DBT@M** (yellow line: λ_{ex} = 365 nm; blue line: λ_{ex} = 430 nm). The black line represents the fluorescence spectrum of **CSU**, which was normalized according to the fluorescence intensity at 430 nm of the yellow line. [**CSU**] = 5 × 10^{-5} M, [**DBT**] = 5 × 10^{-7} M, respectively.

The antenna effect (AE) was calculated based on the emission spectra using equation S3[S3]:

$$\mathbf{AE = I'_{DA,365} / I_{DA,430} = (I_{DA,365} - I_{D,365}) / I_{DA,430}} \text{ (eq. S3)}$$

Where $\mathbf{I_{DA,365}}$ and $\mathbf{I_{DA,480}}$ are the fluorescence intensities at 557 nm with the excitation of the light-harvesting NPs at 365 nm and at 430 nm, respectively. $\mathbf{I_{D,365}}$ is the fluorescence intensities at 557 nm of the NPs of **CSU**, which was normalized with the **DBT@CSU** assembly at 430 nm.

The antenna effect value was calculated as 37.1 in water, measured under the condition of [**CSU**] = 5 × 10^{-5} M, and [**DBT**] = 1.67×10^{-7} M, respectively.

Table S4. Antenna effect with different donor acceptor ratio.

Sample	Concentration, respectively	Antenna Effect (AE)
DBT@CSU (**CSU : DBT** = 100 : 1)	[**CSU**] = 5×10^{-5} M [**DBT**] = 5×10^{-7} M	22.7
DBT@CSU (**CSU : DBT** = 150 : 1)	[**CSU**] = 5×10^{-5} M [**DBT**] = 3.33×10^{-7} M	29.4

DBT@CSU (**CSU : DBT** = 200 : 1)	[**CSU**] = 5×10^{-5} M [**DBT**] = 2.5×10^{-7} M	33.7
DBT@CSU (**CSU : DBT** = 300 : 1)	[**CSU**] = 5×10^{-5} M [**DBT**] = 1.67×10^{-7} M	37.1
DBT@CSU (**CSU : DBT** = 500 : 1)	[**CSU**] = 5×10^{-5} M [**DBT**] = 1×10^{-7} M	33.5
DBT@CSU (**CSU : DBT** = 750 : 1)	[**CSU**] = 5×10^{-5} M [**DBT**] = 6.67×10^{-8} M	28.9
DBT@CSU (**CSU : DBT** = 1000 : 1)	[**CSU**] = 5×10^{-5} M [**DBT**] = 5×10^{-8} M	25.6
DBT@CSU (**CSU : DBT** = 1500 : 1)	[**CSU**] = 5×10^{-5} M [**DBT**] = 3.33×10^{-8} M	23.0

6. Control experiment of light-harvesting by using 5 as donor

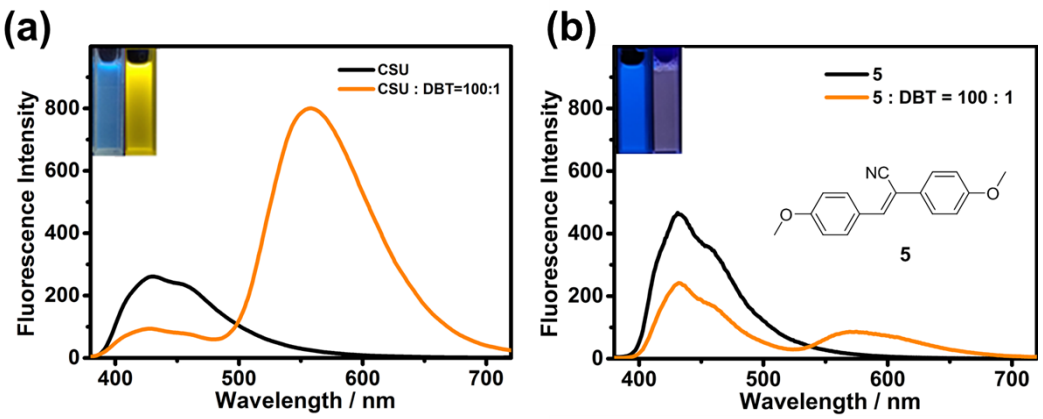


Fig. S4 (a) Fluorescence spectra of **CSU** and **DBT@CSU** upon excitation at 365 nm. (b) Fluorescence spectra of compound **5** and **DBT@5** upon excitation at 365 nm. All these compounds are existed as NPs in water. [**CSU**] = 5×10^{-5} M, [**5**] = 5×10^{-5} M, [**DBT**] = 5×10^{-7} M, respectively.

7. White-light emission with different concentration of DBT

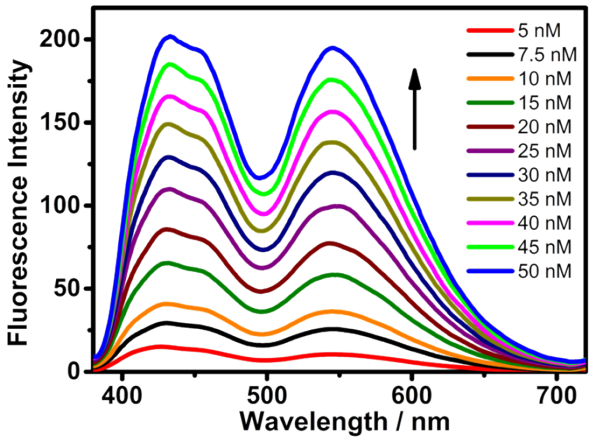


Fig. S5 Fluorescence spectra of **DBT@CSU** (D/A = 1000/1) with different **DBT** concentrations.

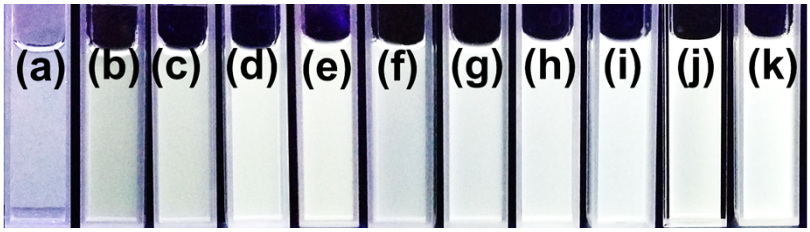


Fig. S6 Fluorescence images: different concentration of **DBT@CSU** nanoparticles (**CSU** : **DBT** = 1000 : 1). [**DBT**] = (a) 5 nM, (b) 7.5 nM, (c) 10 nM, (d) 15 nM, (e) 20 nM, (f) 25 nM, (g) 30 nM, (h) 35 nM, (i) 40 nM, (j) 45 nM, (k) 50 nM.

8. Using different dyes for light-harvesting

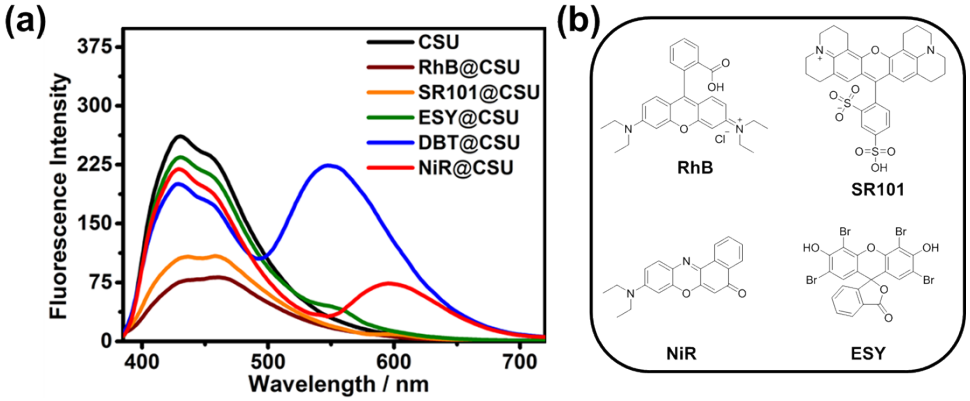
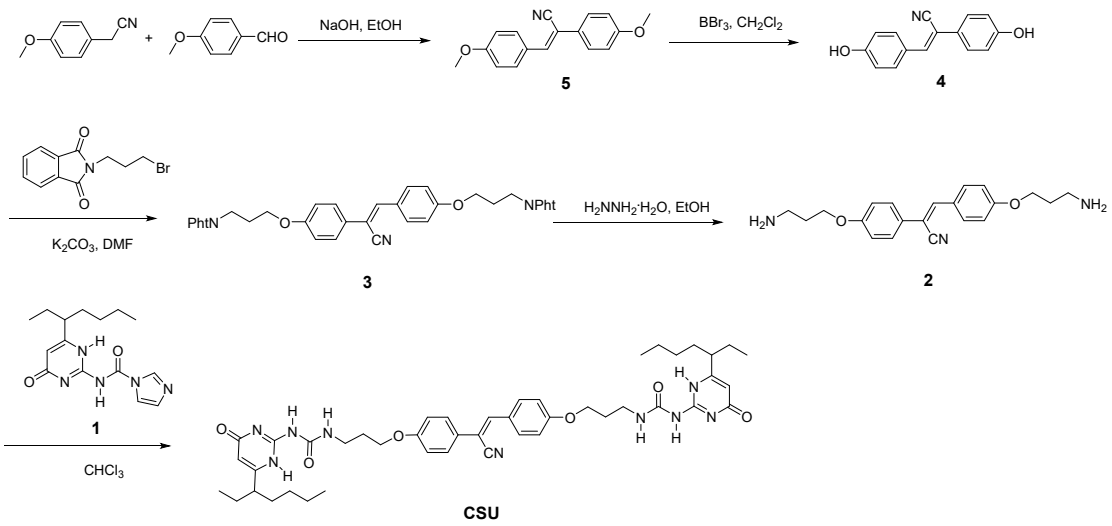


Fig. S7 (a) Fluorescence spectra of **CSU**, **RhB@CSU**, **SR101@CSU, ESY@CSU, DBT@CSU, NiR@CSU** upon excitation at 365 nm. [**CSU**] = 5×10^{-5} M, [**RhB**] = [**SR101**] = [**ESY**] = [**DBT**] = [**NiR**] = 5×10^{-8} M, respectively. (b) The chemical structures of **RhB**, **SR101**, **NiR**, and **ESY**.

9. Synthesis of CSU



Scheme S1. Synthesis of **CSU**

Synthesis of compound 5

To a flask equipped with a magnetic stirrer, 4-Methoxyphenylacetonitrile (1.54 g, 10.5 mmol), p-Anisaldehyde (1.43 g, 10.5 mmol), NaOH (0.42 g, 10.5 mmol) and Ethanol (100 mL) were charged under an argon atmosphere. This mixture was stirred at room temperature for 12 h. After that, a large amount of deionized water was added into the reaction mixture and obtained crude product. The precipitate was separated by filtration and the then washed with deionized water to afford compound **5** as yellowish green solid (2.71 g, 10.2 mmol, 97 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.85 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.58 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 7.36 (s, 1H, alkene-*H*), 6.98-6.94 (m, 4H, Ar-*H*), 3.87 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3).

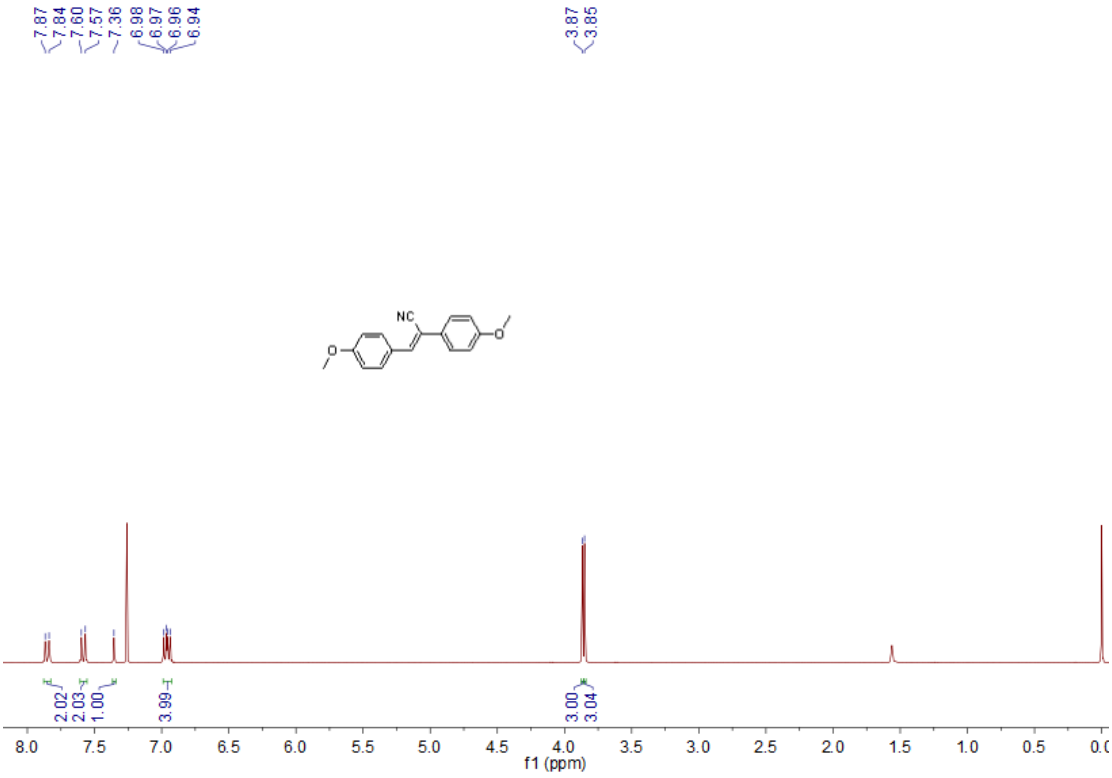


Fig. S8 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound **5**.

Synthesis of compound 4

To a flask equipped with a magnetic stirrer, compound **5** (2.71 g, 10.2 mmol) and dichloromethane (200 mL) were charged under an argon atmosphere. The mixture was cooled to 0 °C and then BBr_3 (10.22 g, 40.8 mmol) was added with vigorous stirred over 15 min. After the system was warmed to room temperature, the reaction was stirred overnight. The solution was cooled in an ice bath, quenched with water (50 mL), The quenched reaction was diluted with dichloromethane (3 × 50 mL) and extracted with 1 M NaOH twice. The aqueous layer was acidified with concentrated HCl and extracted with EtOAc (2 × 100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated to afford compound **4** as a yellowish white solid (2.18 g, 9.2 mmol, 90%). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 10.12 (s, 1H, O*H*), 9.85 (s, 1H, O*H*), 7.79 (d, J = 8.7 Hz, 2H, Ar-*H*), 7.67 (s, 1H, alkene-*H*), 7.52 (d, J = 8.7 Hz, 2H, Ar-*H*), 6.90-6.84 (m, 4H, Ar-*H*).

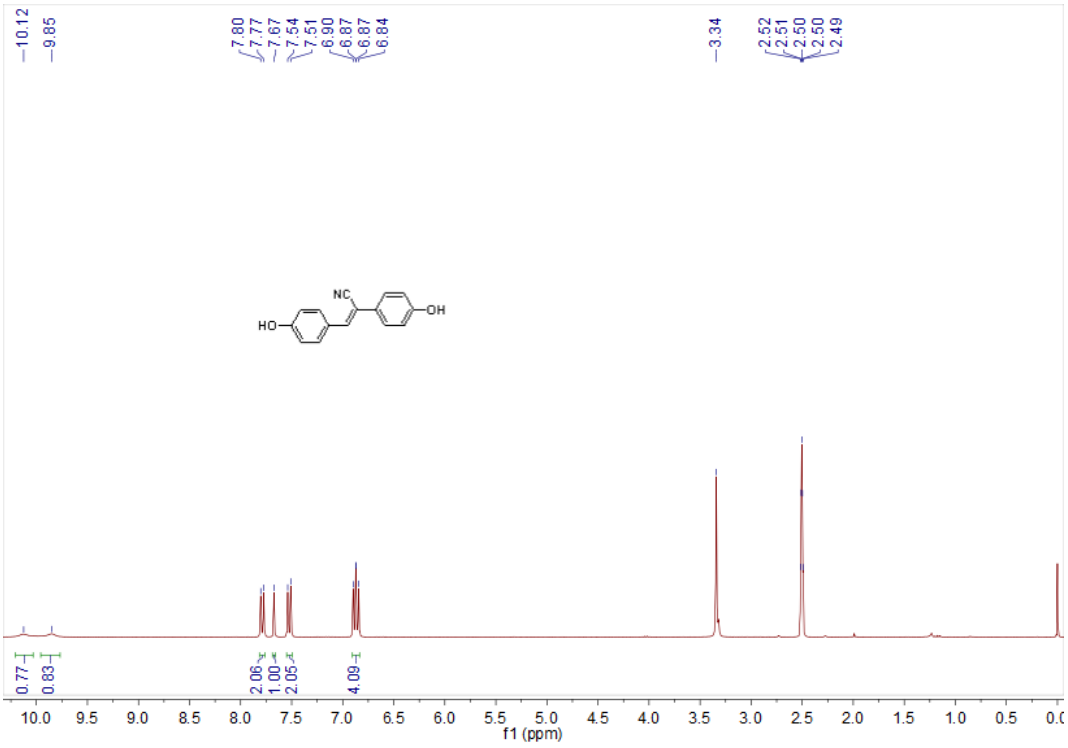


Fig. S9 ^{1}H NMR spectrum (300 MHz, DMSO-d_6, 298 K) of compound **4**.

Synthesis of compound 3

To a flask equipped with a magnetic stirrer, compound **4** (2.18 g, 9.2 mmol), K_2CO_3 (3.81 g, 27.6 mmol), and DMF (100 mL) were charged under an argon atmosphere. The mixture was stirred at room temperature for 0.5 h. The *N*-(3-bromopropyl)phthalimide (6.17 g, 23.0 mmol) was added into the mixture. The mixture was stirred at 120 °C overnight. After the system was cooled to room temperature and the reaction was quenched by adding water. The reacted mixture was extracted with dichloromethane. The organic layer was dried with anhydrous Na_2SO_4. The crude product was purified by silica gel chromatography (hexane : dichloromethane = 5 : 1, *v/v*) to afford the product as a yellowish white solid (4.95 g, 8.1 mmol, 88 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.86-7.83 (m, 4H, Ar-*H*), 7.78 (d, *J* = 8.7 Hz, 2H, Ar-*H*),7.74-7.71 (m, 4H, Ar-*H*), 7.51 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 7.31 (s, 1H, alkene-*H*), 6.86-6.82 (m, 4H, Ar-*H*), 4.11-4.05 (m, 4H, OCH_2), 3.93 (t, *J* = 6.6 Hz, 4H, NCH_2), 2.23-2.19 (m, 4H, $CH_2CH_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 168.4, 160.2, 159.2, 139.9, 134.0, 132.2, 130.8, 127.5, 127.0, 126.8, 123.3, 118.6, 114.9, 114.7, 108.3, 65.9, 35.4, 28.2. HR-ESI-MS: *m/z* calcd for $C_{37}H_{30}N_3O_6$ $[M + H]^+$= 612.2129, found = 612.2128.

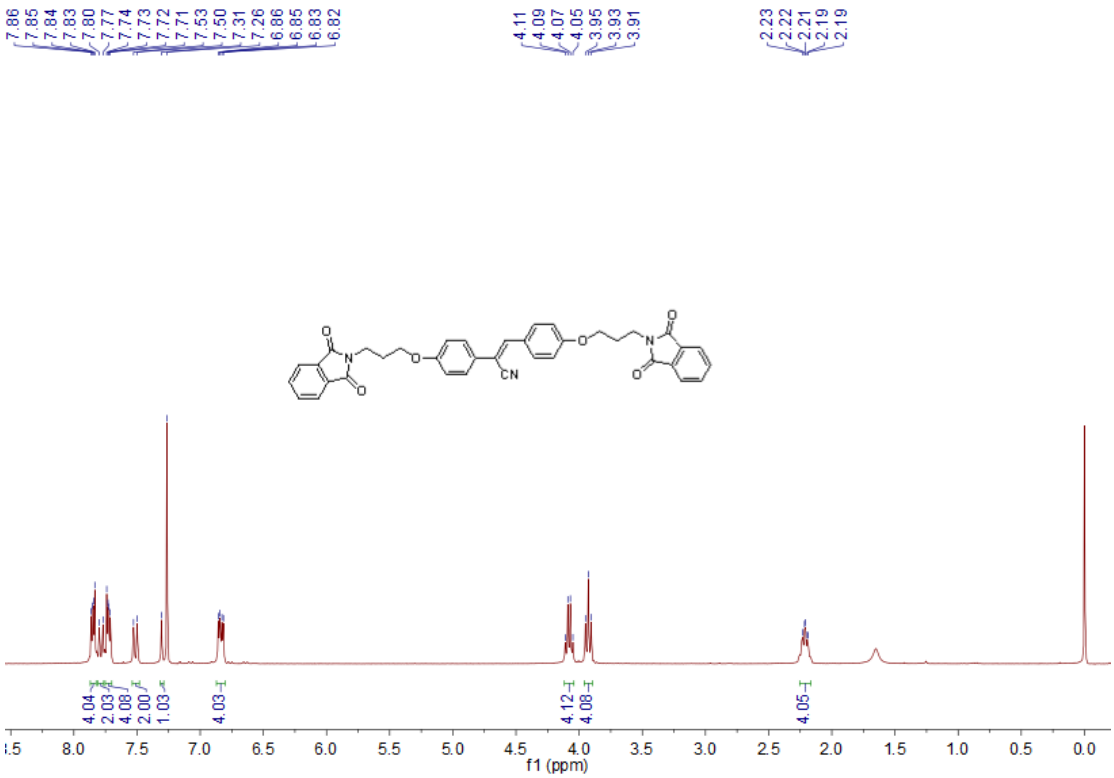


Fig. S10 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound **3**.

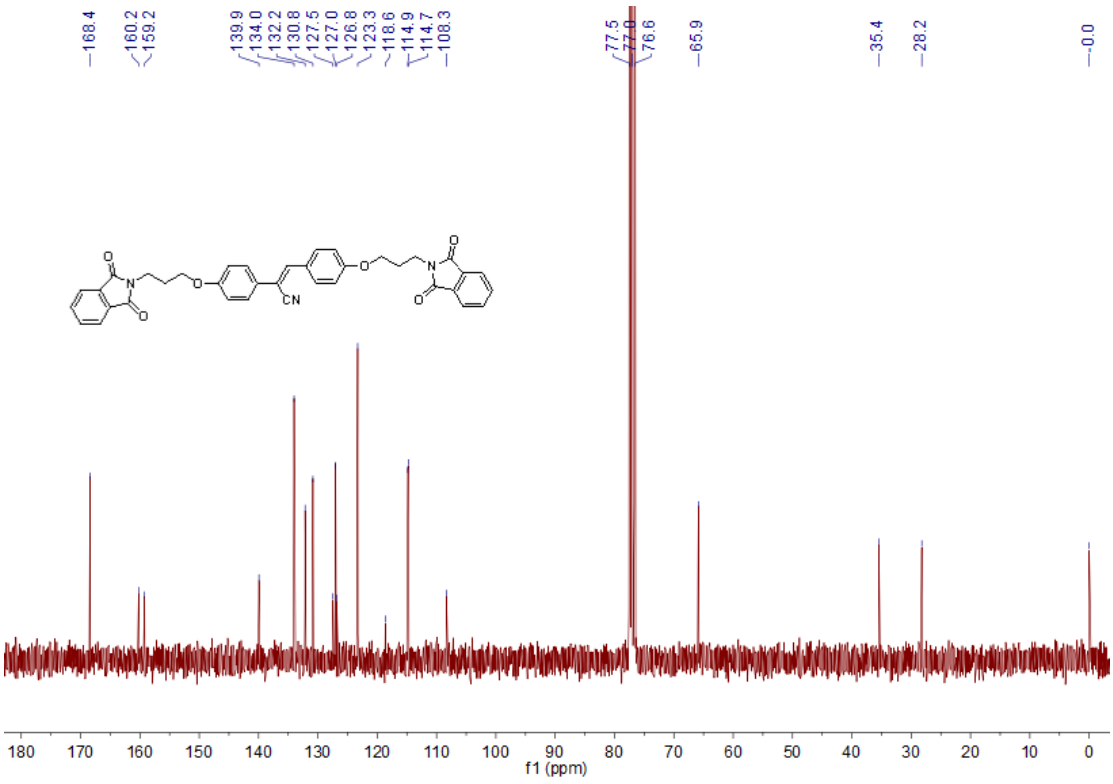


Fig. S11 ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of compound **3**.

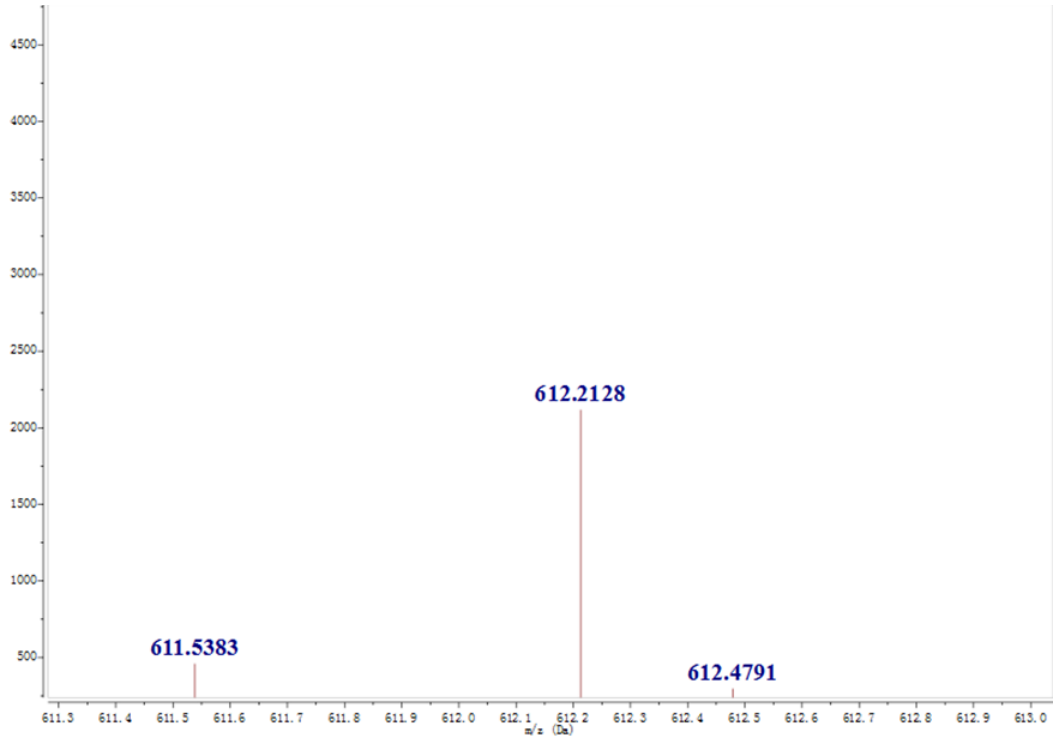


Fig. S12 HR-MS (ESI, positive mode, CH_3CN) of **3**.

Synthesis of compound 2

To a solution of **3** (4.95 g, 8.1 mmol) in EtOH (200 mL) was added hydrazine monohydrate (20 mL) and the mixture was then refluxed for 12 h under N_2 atmosphere. The solvent was removed under vacuum. The residue was dissolved in water (60 mL) and the resulting mixture was extracted with dichloromethane (2 × 100 mL). The combined extracts were washed with brine, and the organic layer was dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the product as a green solid (1.62 g, 4.6 mmol, 57 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.84 (d, J = 8.7 Hz, 2H, Ar-*H*), 7.57 (d, J = 9.0 Hz, 2H, Ar-*H*), 7.35 (s, 1H, alkene-*H*), 6.98-6.93 (m, 4H, Ar-*H*), 4.14-4.08 (m, 4H, OCH_2), 2.93 (t, J = 6.6 Hz, 4H, NCH_2), 1.98-1.91 (m, 4H, $CH_2CH_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 160.5, 159.5, 139.9, 130.9, 127.4, 127.1, 126.7, 118.7, 114.9, 114.8, 108.3, 66.1, 66.0, 39.2, 39.1, 32.9, 32.9. HR-ESI-MS: *m/z* calcd for $C_{12}H_{26}N_3O_2$ $[M + H]^+$ = 352.2020, found =352.2019.

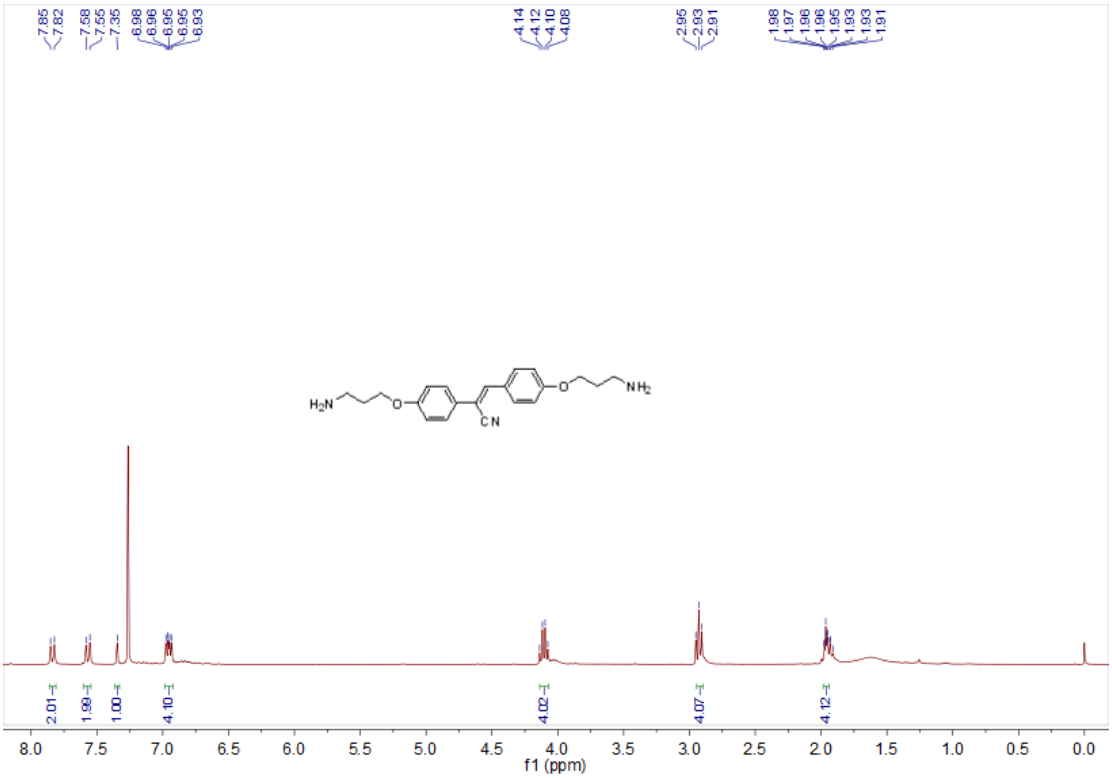


Fig. S13 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound **2**.

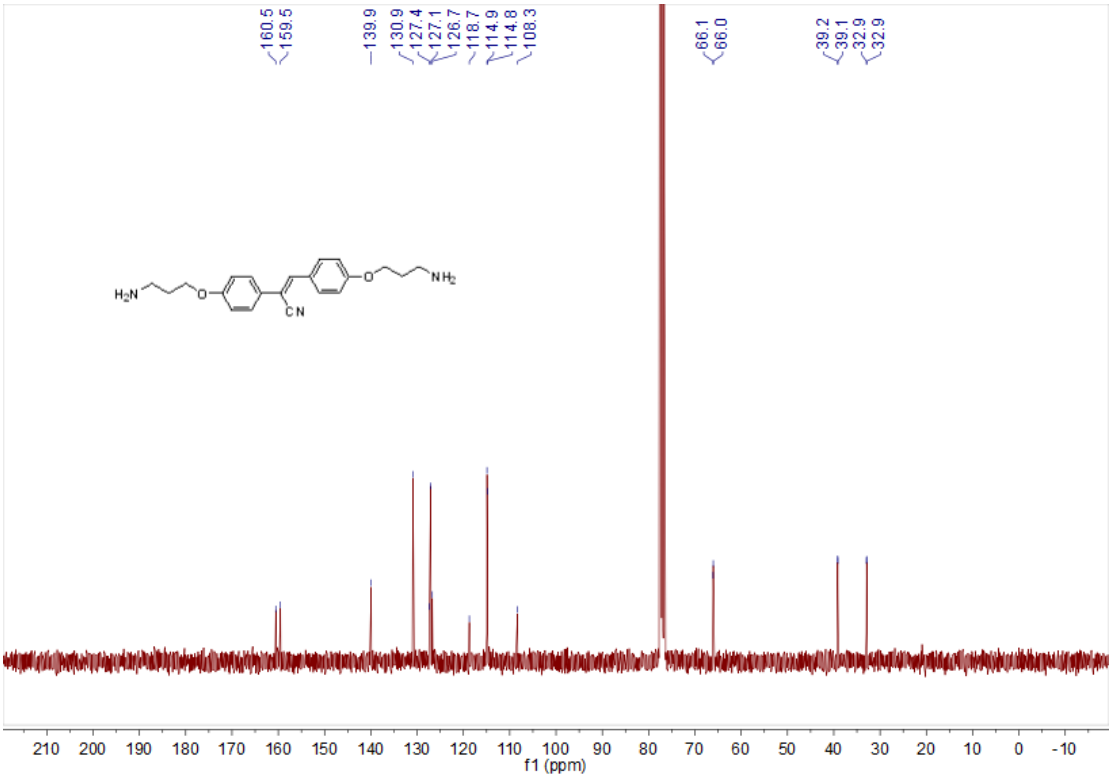


Fig. S14 ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of compound **2**.

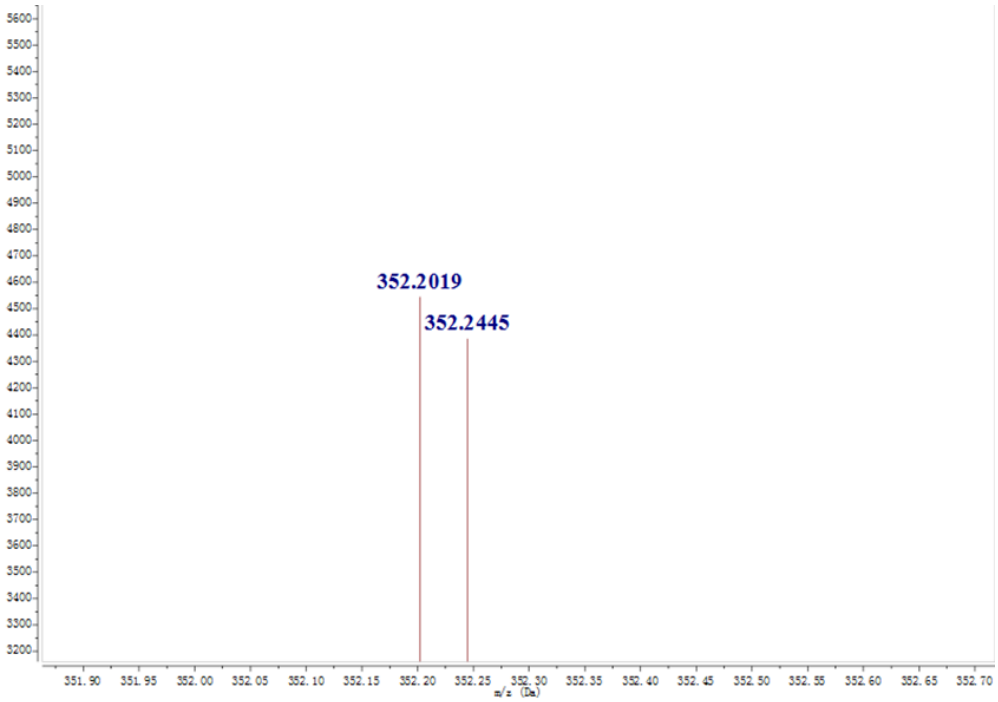


Fig. S15 HR-MS (ESI, positive mode, CH_3OH) of **2**.

Synthesis of compound CSU

UPy precursor **1** (3.06 g, 10.1 mmol) and compound **2** (1.62 g, 4.6 mmol) were dissolved in dry $CHCl_3$ (100 mL) and this solution was stirred for 12 h under nitrogen at room temperature. To the reaction mixture $CHCl_3$ (20 mL) was added and the organic layer was washed with 1 M HCl (50 mL), saturated $NaHCO_3$ (50 mL), brine (50 mL), dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (dichloromethane : methanol = 100 : 1, *v*/*v*) to afford the product as a white solid (2.20 g, 2.7 mmol, 58 %).^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 13.18 (s, 2H, N-*H*), 11.96 (s, 2H, N-*H*), 10.35 (s, 2H, N-*H*), 7.80 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.53 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.31 (s, 1H, alkene-*H*), 6.97-6.92 (m, 4H, Ar-*H*), 5.78 (s, 2H, alkene-*H*), 4.13-4.07 (m, 4H, OCH_2), 3.51-3.45 (m, 4H, NCH_2), 2.31-2.26 (m, 2H, $CH_3CH_2CHCH_2$), 2.15-2.11 (m, 4H, NCH_2CH_2), 1.66-1.49 (m, 8H), 1.31-1.18 (m, 8H), 0.90-0.83 (m, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 173.2, 160.6, 159.6, 156.9, 155.6, 154.8, 139.8, 130.8, 127.2, 126.9, 126.6, 118.7, 115.0, 108.2, 106.3, 65.7, 45.3, 37.0, 32.9, 29.3, 29.1, 26.6, 22.5, 13.9, 11.7. ESI-MS: *m/z* calcd for $C_{45}H_{60}N_9O_6$ $[M + H]^+$ = 822.47, found = 822.25. HR-ESI-MS: *m/z* calcd for $C_{45}H_{58}N_9O_6$ $[M - H]^-$ = 820.4516, found = 820.4506.

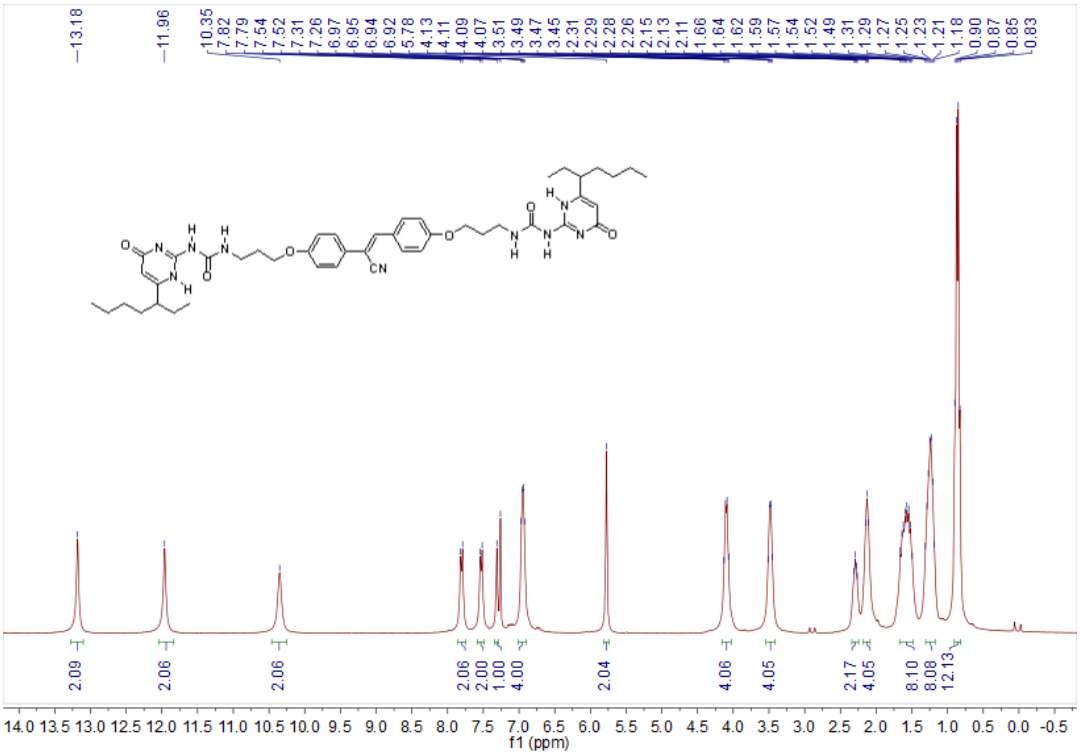


Fig. S16 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **CSU**.

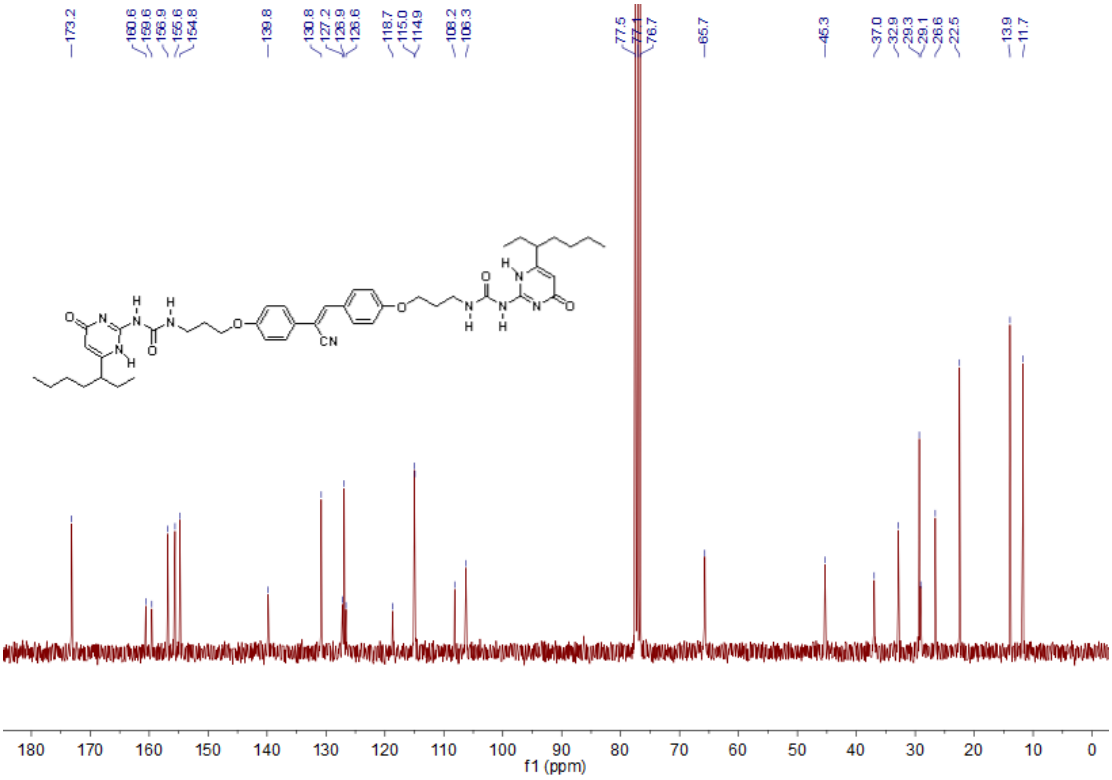


Fig. S17 ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of **CSU**.

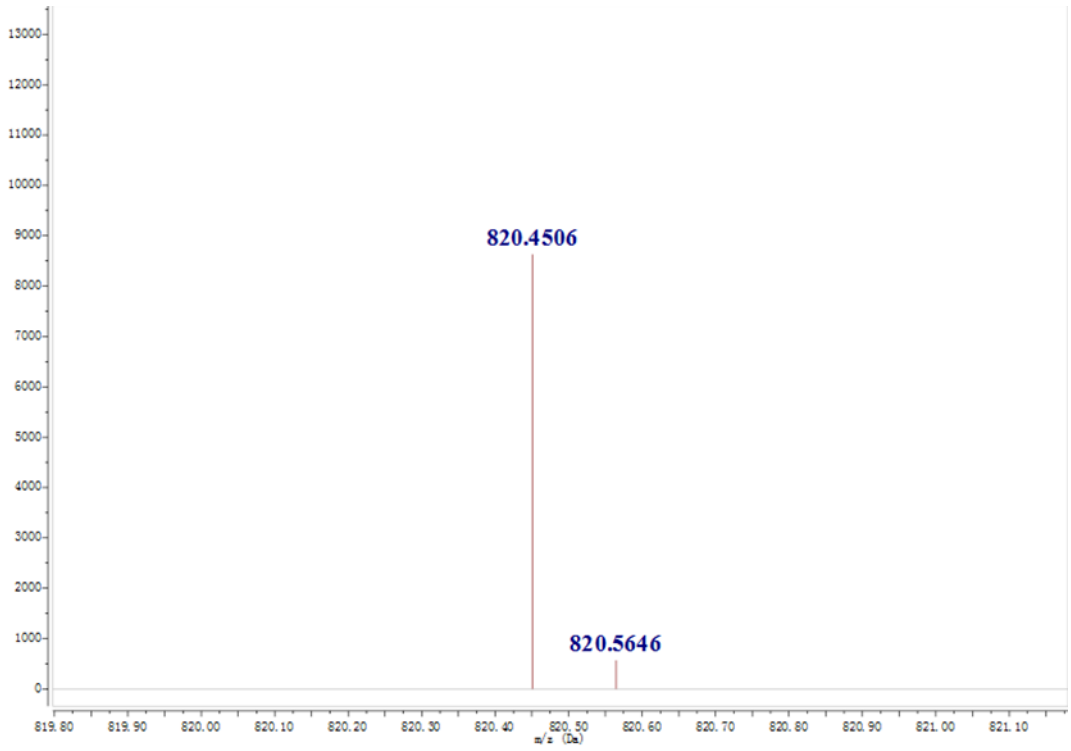
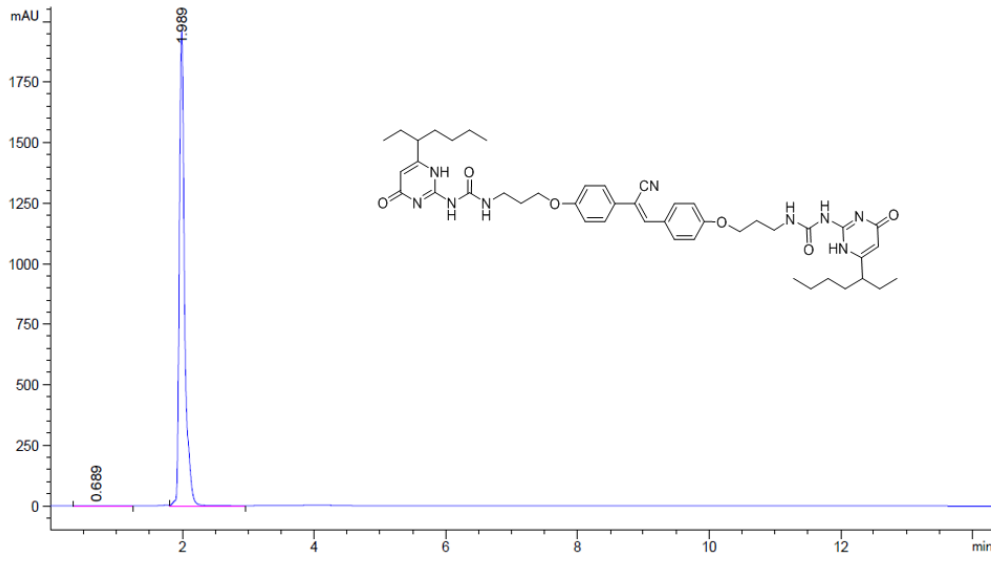


Fig. S18 HR-MS (ESI, negative mode, CH_3CN) of **CSU**.



RT(min)	Area (Mau*s)	Height (mAU)	Width(min)	Area (%)
0.689	4.71	0.25	0.24	0.04
1.989	10974.80	1958.68	0.08	99.96

Fig. S19 HPLC diagram (THF) of **CSU**.

10. References

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[S3] Hao M., Sun G., Zuo M., Xu Z., Chen Y., Hu X-Y., and Wang L., *Angew. Chem. Int. Ed.*, **2020**, *59*, 10095-10100.