Supporting Information

A novel near-infrared electrochromic material based on the electron-induced proton transfer mechanism

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1. General experimental details

Materials

Trifluoroacetic acid (CF_3COOH, TFA), tetrabutylammonium hexafluorophosphate ($TBAPF_6$), N,N-dimethylformamide, phosphorus oxychloride and cyclohexanone were purchased from Energy Chemicals. N,N-dimethylbenzene-1,4-diamine, 1-isocyanato-4-methylbenzene, 2,3,3-trimethyl-4,5-benzindole, 4-bromomethylbenzoic acid, 1,2-dichlorobenzene and anhydrous ethanol were purchased from Adamas-beta Reagent. 1,1,2-trimethyl-1H-benz[e]indole, acetonitrile and tetrahydrofuran were purchased from Aladdin Chemicals. The base and curing agent of polydimethylsiloxane (PDMS) were purchased from Dow Corning. The ITO glass electrodes were purchased from South China Xiang Science & Technology company. All the solvents were used as received without any further purification. $TBAPF_6$ was recrystallized for three times in anhydrous ethanol and dried under vacuum overnight at 80 °C before using in the electrochemical measurements.

Characterizations

Optical absorption spectra were measured using a UV-Vis double-beam spectrophotometer (UV-2600i Plus, SHIMADZU). The electrochemical data were obtained from Bio-logic SP-150e electrochemical work station. ^1H, ^{13}C and Cozy NMR spectra were measured by a Bruker AVANCE NEO 400 M NMR spectrometer. Chemical shift values were given relative to tetramethylsilane (TMS). Mass spectral (MS) analysis was obtained by an Agilent 1200/G6100A Mass Spectrometer. Infrared (IR) spectra studies were performed on a Vertex 80/80V FT-IR spectrometer with LN-MCT Mid DC detector over the range of 4000-400 cm^{-1} using a KBr plate.

Electrochemical measurements

Cyclic voltammetry (CV) measurements of the functional molecules or mixtures in this research were performed using a three-electrode system containing $TBAPF_6$ (0.1 mol/L) in acetonitrile as the supporting electrolyte. And, the three-electrode system contained a glass-carbon working electrode (IDA, China) as the working electrode, a Pt wire as the counter electrode (IDA, China), and an Ag wire as the reference electrode (IDA, China).

Preparation of PDMS film and PDMS spacer

Firstly, the base and curer of PDMS were mixed with the weight ratio of 10:1, then the mixture was degassed by a vacuum pump. After the above treatments, the mixture was poured onto a clean glass and heated at 60 °C for 12 h. Finally, the cured PDMS film with the thickness of 0.26 mm was prepared. And, the PDMS spacer with specific patterns could be formed by a scissor.

Fabrication of the EC devices

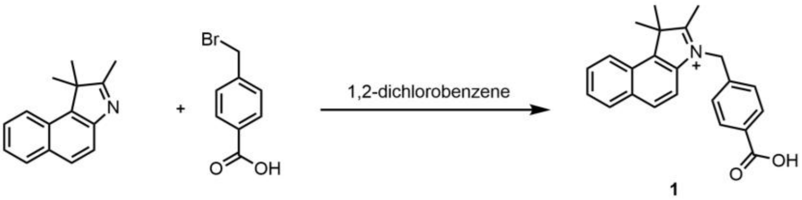
The structure of liquid electrochromic device was shown in Figure 4a. The functional solution contained 2×10^{-4} mol/L acid-responsive NIR molecule (CY-N), 2×10^{-3} mol/L Urea-N, 1×10^{-3} mol/L p-BQ and 0.1 mol/L $TBAPF_6$ in 5 mL acetonitrile. The cured PDMS (thickness=0.26 mm) with a hole in center (area=2.5 cm×2.5 cm=6.25 cm^2) as the spacer was put between two ITO glasses (each area=3.0 cm× 3.0 cm=9.00 cm^2). Then, the functional solution was injected into the spacer and the liquid device was fabricated finally.

Synthesis of the Urea-N

Scheme S1. Synthetic route of the molecule Urea-N.

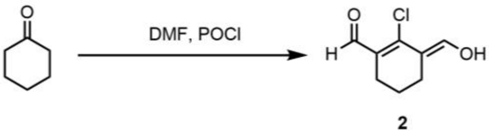
Detailed synthetic process of Urea-N was reported in the previous work (Adv. Sci., 2022, 9, 2202236). The characterization was shown below (**Figure S3 to S6**). ^1H NMR (400 MHz, DMSO) δ 8.38 (s, 1H), 8.22 (s, 1H), 7.31 (d, J= 8.4 Hz, 2H), 7.24 (d, J = 9.0 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 6.69 (d, J = 9.0 Hz, 2H), 2.82 (s, 6H), 2.23 (s, 3H).

Synthesis of the Cy-N



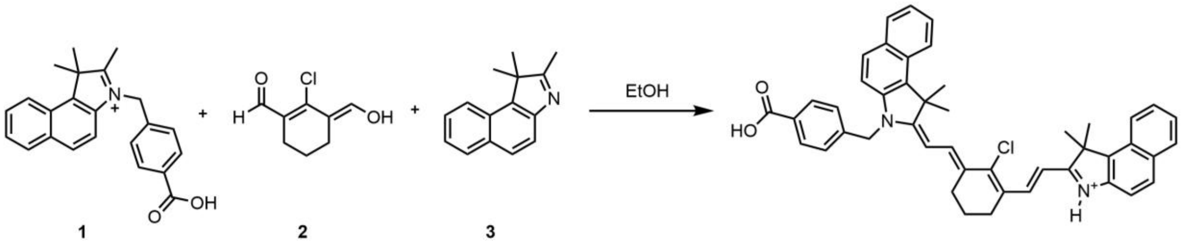
Scheme S2. Synthetic route of the molecule 1.

In a 100 mL round-bottom flask, 2,3,3-trimethyl-4,5-benzindole (5.0 g, 24 mmol) and 4-bromomethylbenzoic acid (6.1 g, 28 mmol) were added, followed by the addition of 20 mL of 1,2-dichlorobenzene. The reaction mixture was then heated in an oil bath at 110 °C for 4 hours. After the reaction was complete, the system was allowed to cool to room temperature. The mixture was filtered through a Buchner funnel, and the filter cake was washed with methanol to purify the product. The solid was then dried to yield a grayish-white solid (3.4 g, 41%).



Scheme S3. Synthetic route of molecule 2.

In a 250 mL round-bottom flask at 0 °C, 25 mL of N, N-dimethylformamide was added, followed by the dropwise addition of 17.5 mL of phosphorus oxychloride. After the addition was complete, the reaction was allowed to proceed at 0°C for 30 minutes. Then, 5 mL of cyclohexanone was added, and the mixture was subsequently heated in an oil bath at 60°C for 4 hours. The reaction mixture was then poured into 100 mL of ice water and allowed to react for 5 hours, resulting in a turbid suspension. The mixture was filtered through a Buchner funnel, washed with water, followed by washing with ether, and then dried to yield a gray-green solid (3.4 g, 39%).



Scheme S4. Synthetic route of the molecule Cy-N.

In a 250 mL round-bottom flask, Compound 1 (3.4 g, 10 mmol), Compound 2 (1.7 g, 10 mmol), and Compound 3 (2.1 g, 10 mmol) were added, followed by the addition of 100 mL of ethanol. The reaction mixture was then heated in an oil bath at 50 °C for 5 hours. After the reaction was complete, the mixture was directly concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient elution (PE: EA = 10:1 → 2:1), yielding a reddish-brown solid (800 mg, 12%). The solid was further purified by recrystallization from methanol, and after drying, a reddish-brown solid was obtained (500 mg, 7%). The characterization was shown below (**Figure S6 to S10**). ^{1}H NMR (400 MHz, DMSO) δ 12.91 (s, 1H), 8.24 (d, J = 15.6 Hz, 1H), 8.13 (dd, J = 8.3, 4.9 Hz, 2H), 8.01 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 3H), 7.87 (d, J = 8.2 Hz, 1H), 7.81 (dd, J = 12.9, 8.7 Hz, 2H), 7.62 - 7.56 (m, 2H), 7.53 (d, J = 4.4 Hz, 1H), 7.48 (dd, J = 13.9, 6.8 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.9 Hz, 1H), 7.31 - 7.24 (m, 1H), 6.73 (d, J = 15.7 Hz, 1H), 5.58 (d, J = 12.7 Hz, 1H), 5.24 (s, 2H), 2.62 (t, J = 5.7 Hz, 2H), 2.47 - 2.36 (m, 2H), 1.96 (s, 6H), 1.77 - 1.71 (m, 2H), 1.57 (s, 6H).

2. Supplementary Figures

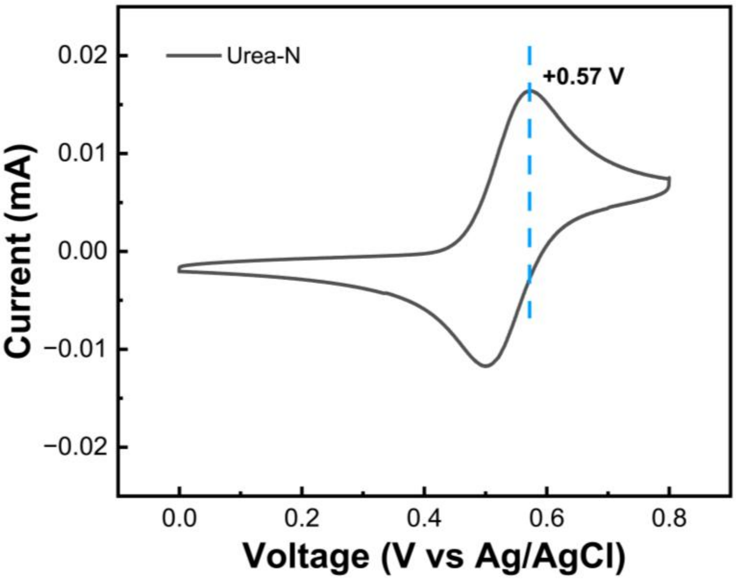


Figure S1. Cyclic voltammetry diagrams of 1.0×10^{-3} mol/L Urea-N with 0.1 mol/L $TBAPF_6$ in CH_3CN.

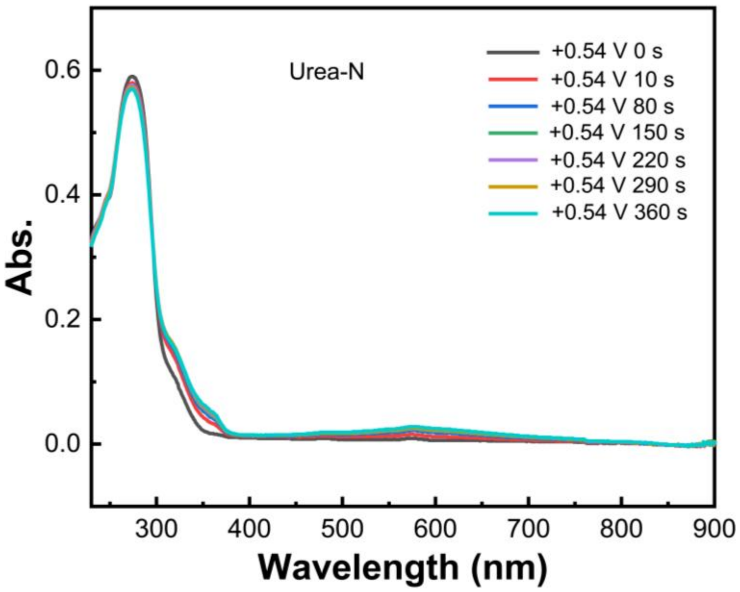


Figure S2. UV-Vis-NIR absorption spectra of 5.0×10^{-4} mol/L Urea-N with 0.1 mol/L $TBAPF_6$ in CH_3CN, when a voltage (+0.54 V) was applied with various time.

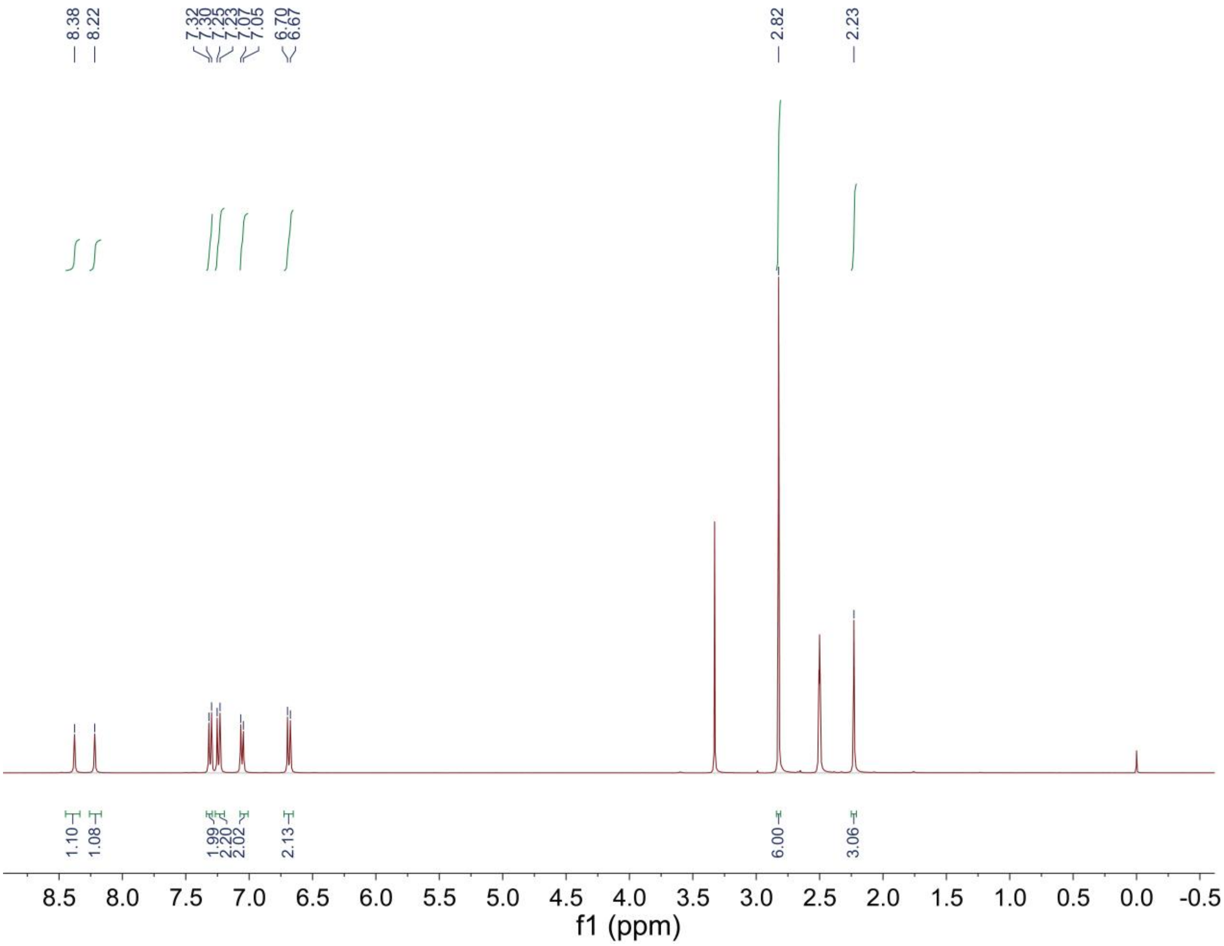


Figure S3. ^{1}H NMR spectrum of Urea-N in deuterated DMSO recorded at 400 MHz at room temperature.

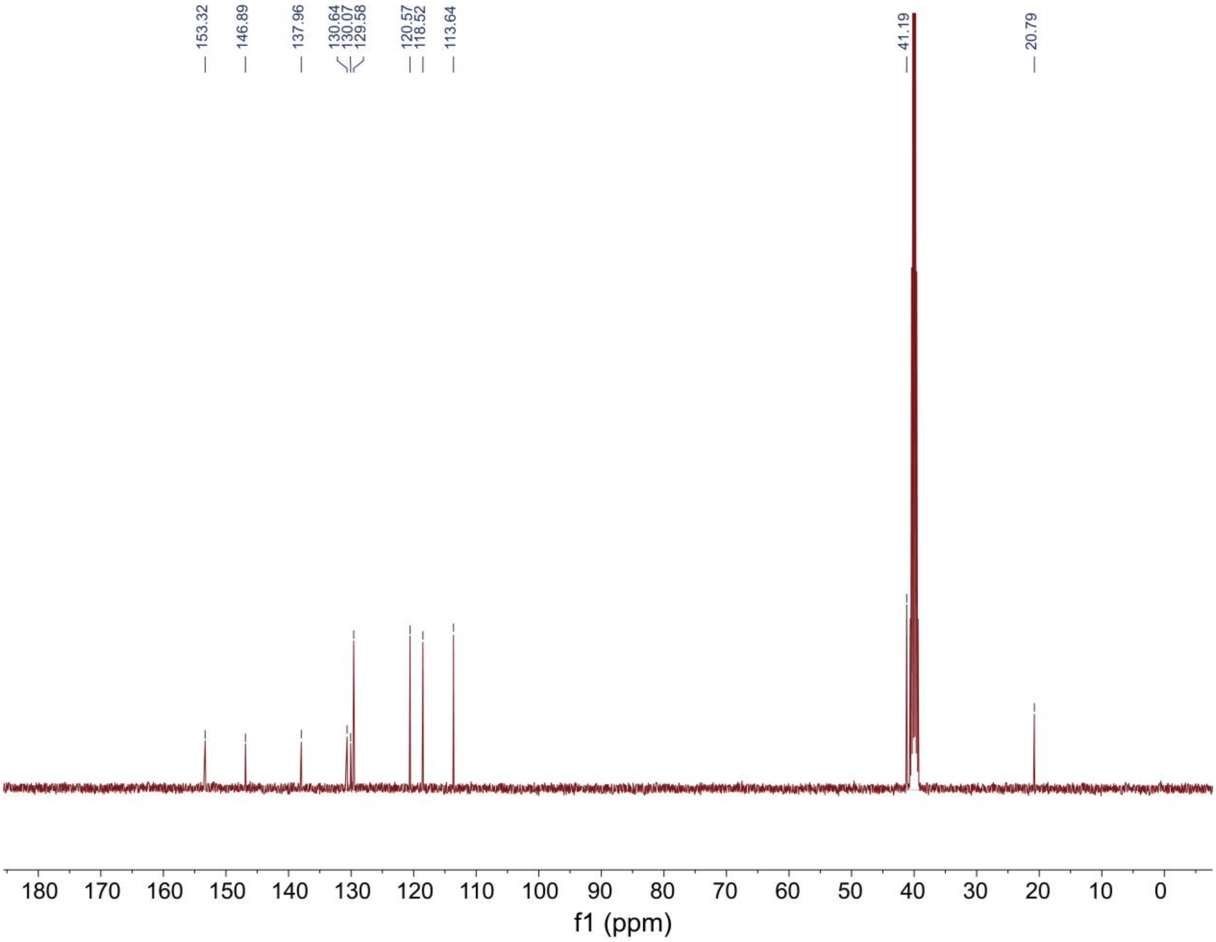


Figure S4. ^{13}C NMR spectrum of Urea-N in deuterated DMSO recorded at 400 MHz at room temperature.

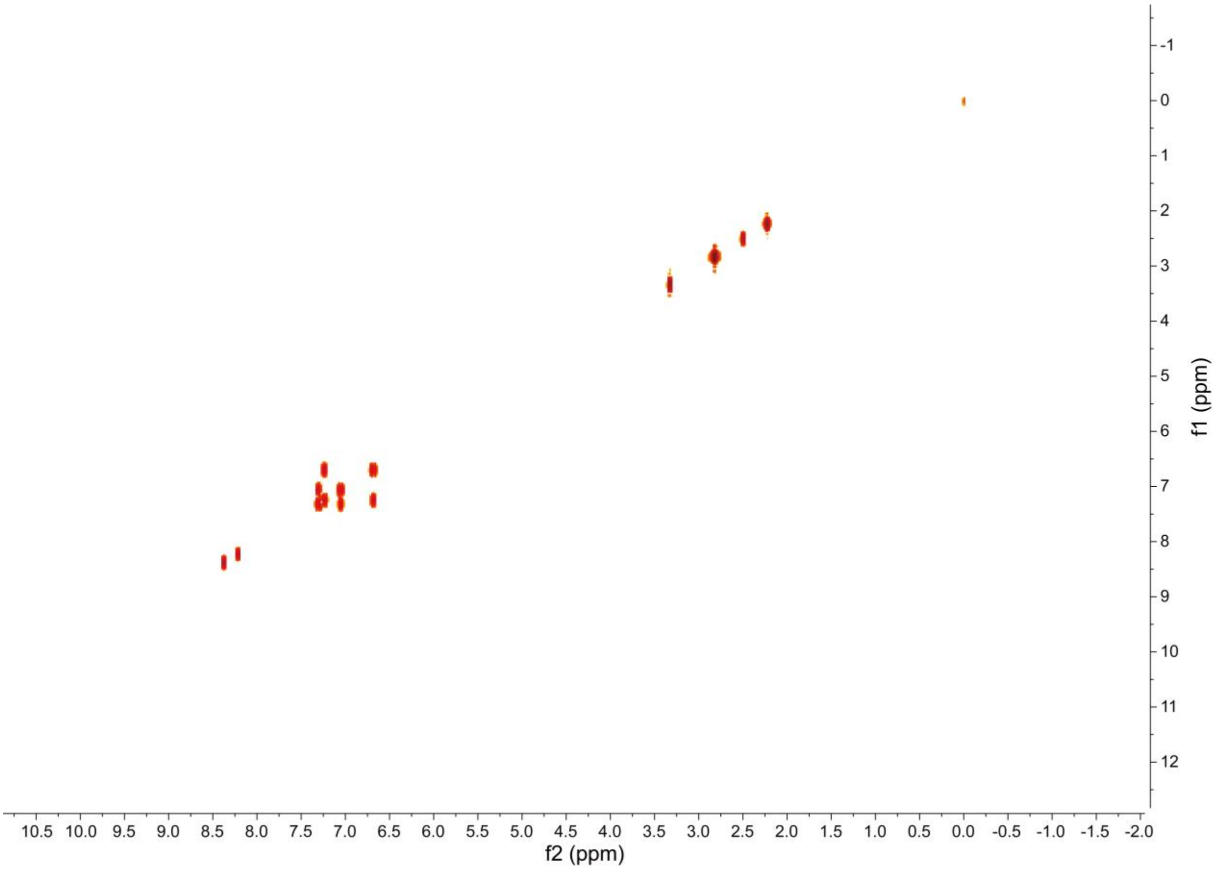


Figure S5. ^{1}H Cosy NMR spectrum of Urea-N in deuterated DMSO recorded at 400 MHz at room temperature.

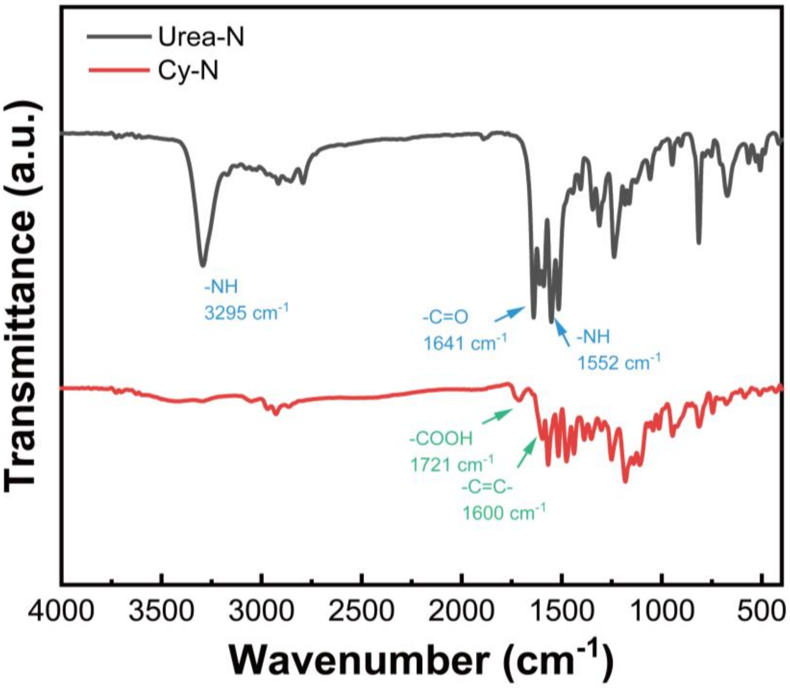


Figure S6. IR spectra of Urea-N and Cy-N.

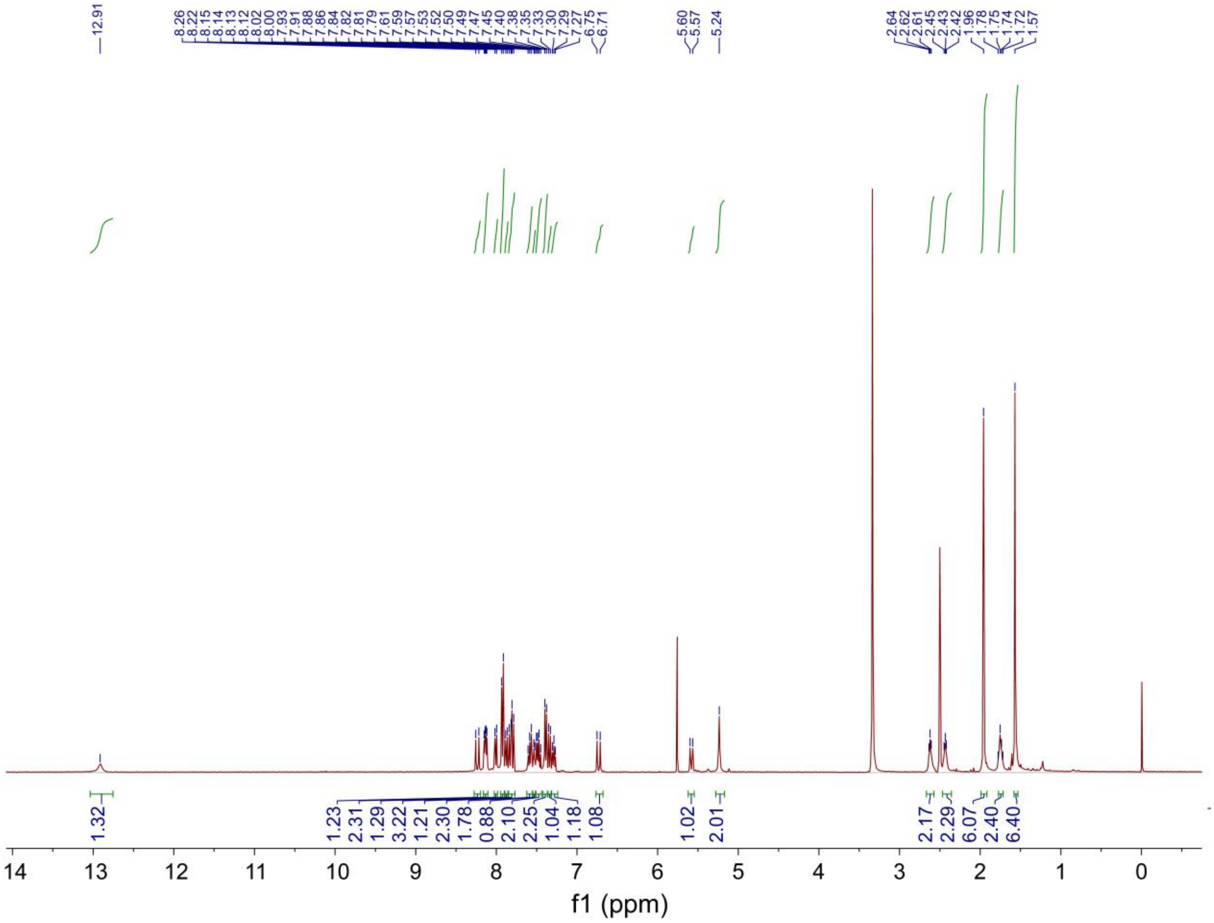


Figure S7. ^{1}H NMR spectrum of Cy-N in deuterated DMSO recorded at 400 MHz at room temperature.

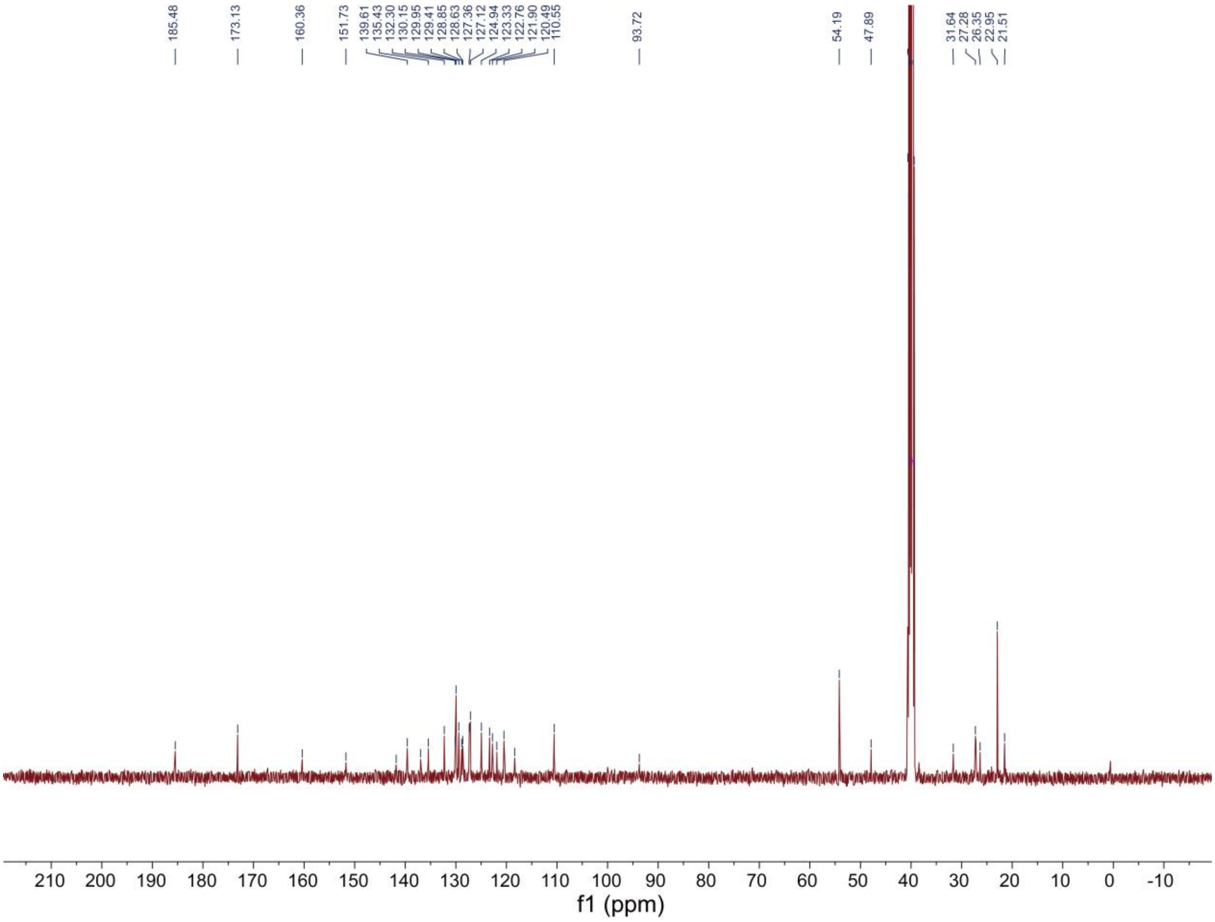


Figure S8. ^{13}C NMR spectrum of Cy-N in deuterated DMSO recorded at 400 MHz at room temperature.

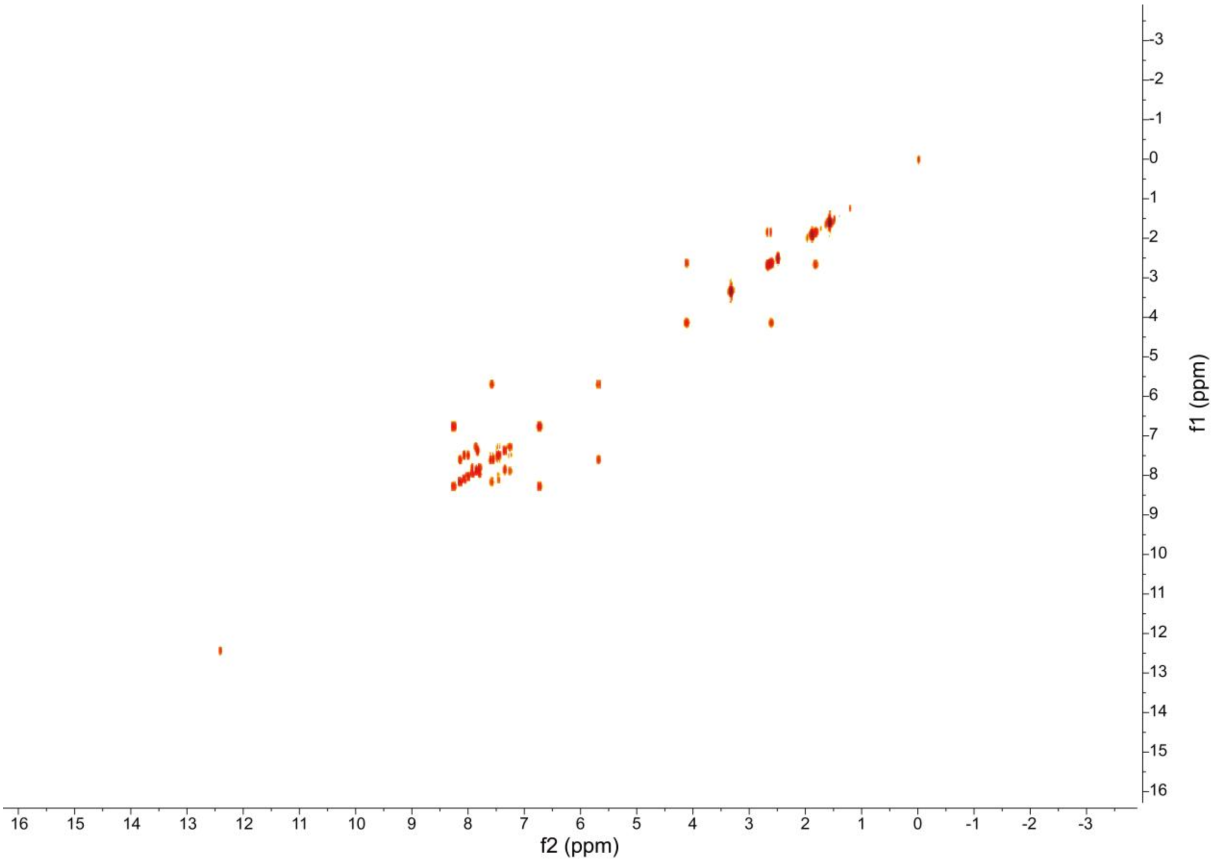


Figure S9. ^{1}H Cosy NMR spectrum of Cy-N in deuterated DMSO recorded at 400 MHz at room temperature.

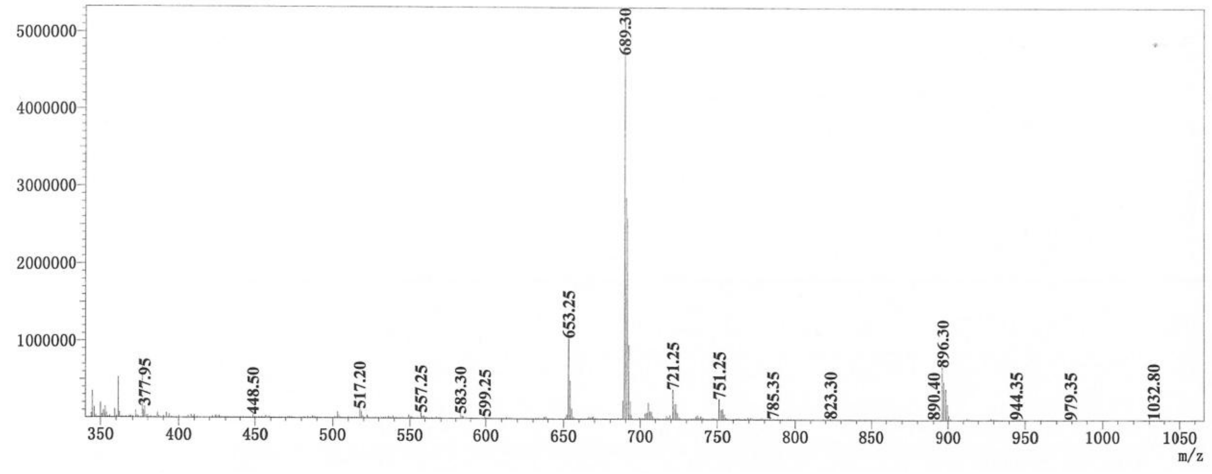


Figure S10. Mass spectrum of the Cy-N.