

*Supporting information*

Unexpected Fluorescence From Polymers Containing  
Dithio/Amino-Succinimides

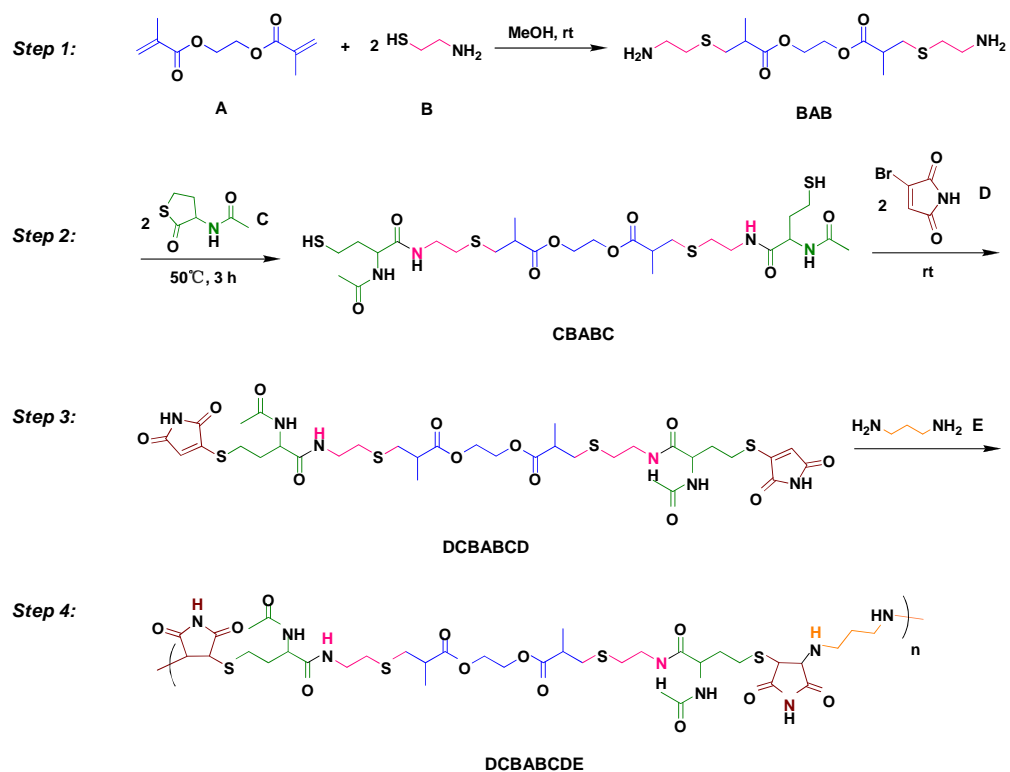
Jun-Jie Yan,<sup>\*,†</sup> Bin Zheng,<sup>‡</sup> Dong-Hui Pan,<sup>†</sup> Run-Lin Yang,<sup>†</sup> Yu-Ping Xu,<sup>†</sup> Li-Zhen Wang,<sup>†</sup> Min Yang<sup>\*,†</sup>

<sup>†</sup> Molecular Imaging Center, Key Laboratory of nuclear medicine, Ministry of Health, Jiangsu Key Laboratory of Molecular Nuclear Medicine, Jiangsu Institute of Nuclear Medicine, Wuxi 214063, Jiangsu, P. R. China.

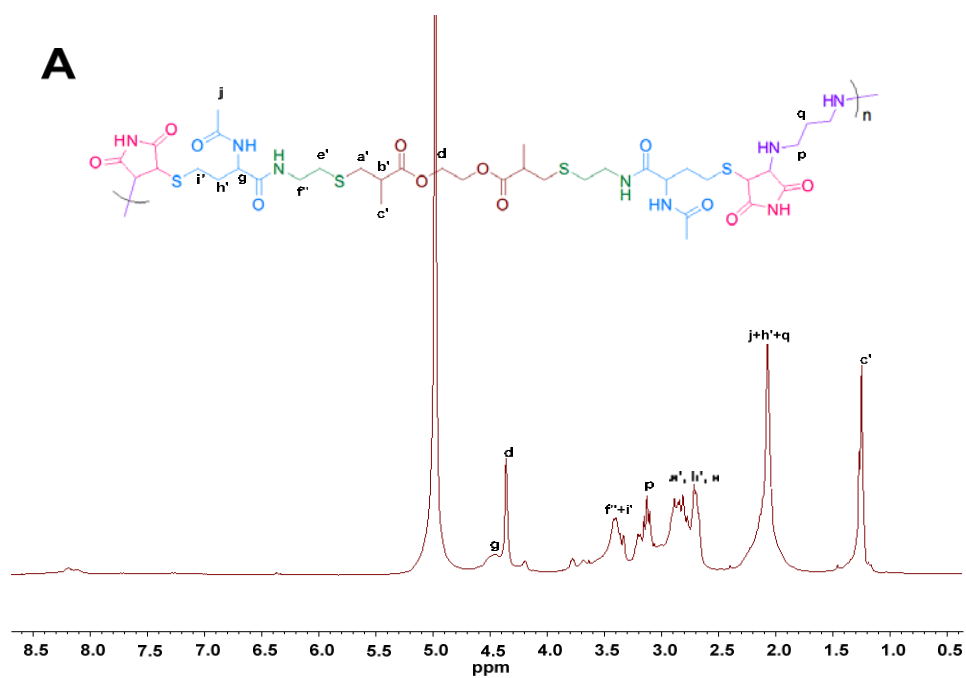
<sup>‡</sup> School of Chemistry and Chemical Engineering, Hefei Normal University, Hefei, 230061, Anhui, P. R. China

*E-mail: yanjunjie@jsinm.org, yangmin@jsinm.org*

**Dynamic fluorescence trace.** The detailed reactions were performed according to our previous work on preparing sequenced copolymers.<sup>1</sup> At the end of each step, a portion of 10  $\mu\text{L}$  solution was taken from the mixture and diluted to 1 mL with DMF, subjecting to fluorescence detection under same conditions. In order to eliminate the salts and unreacted reagents, products were purified by precipitating reaction mixture into diethyl ether, and dried under vacuum for 2 h at room temperature. The purified sequenced copolymer was still dissolved in DMF for fluorescence measurement to ensure complete dissolution.



**Scheme S1.** Detailed reactions for preparing a DCBABCDE-sequenced copolymer.<sup>1</sup>



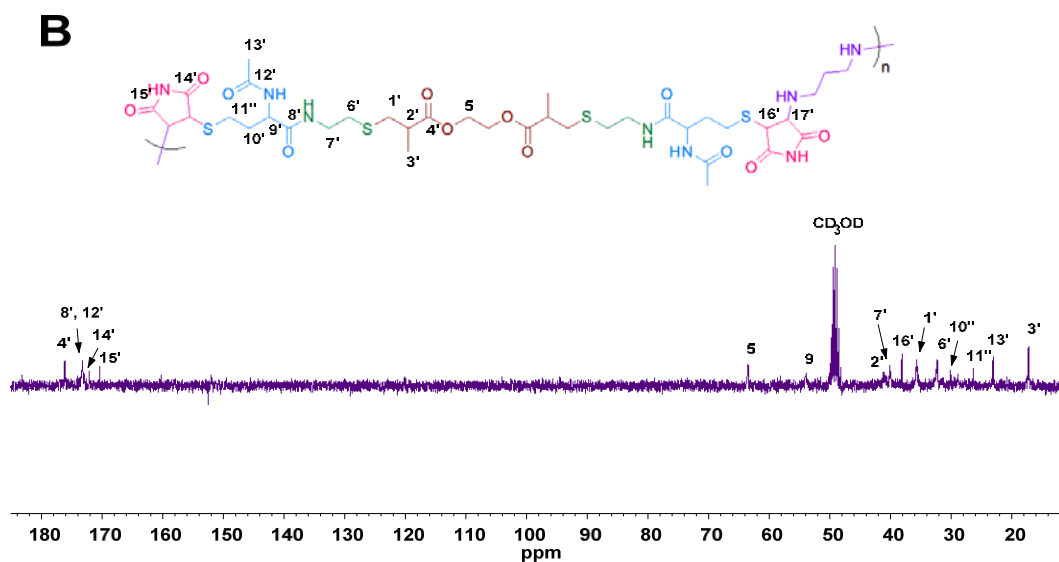
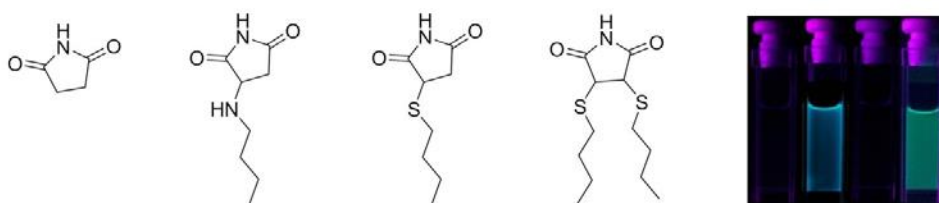
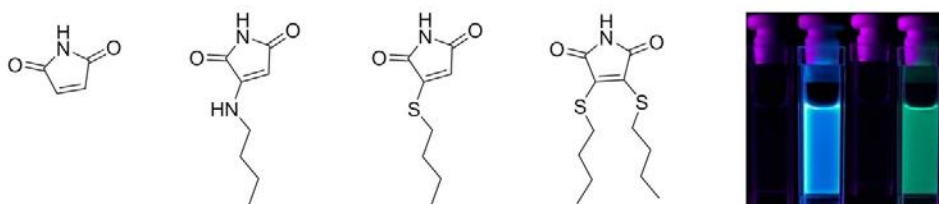


Fig. S1. <sup>1</sup>H NMR spectrum (A) and <sup>13</sup>C NMR spectrum (B) of five sequence-ordered copolymer in CD<sub>3</sub>OD.

**Sulfur/ Nitrogen Substituted Succinimides**

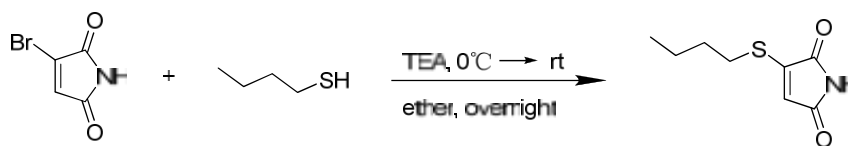


**Homologous Maleimides**



**Scheme S2.** Library of thio/amino succinimides and homologous maleimides and optical properties under UV 365 nm irradiation (1 mg/mL, hexane/ethyl acetate = 3/1).

## Synthesis of 2-(butylthio)-maleimide.<sup>2</sup>



Bromomaleimide (401.2 mg, 2.28 mmol) was dissolved in 15 mL diethyl ether, purged with argon for 10 min. Butanethiol (215.1 mg, 2.38 mmol) was added and stirred for 5 min. The solution was cooled to 0°C in an ice bath. Triethylamine (242.4 mg, 2.40 mmol) was then added dropwise to the cooled solution, white precipitate formed immediately. Upon addition of triethylamine, the mixture was left to room temperature and left to stir overnight. The mixture was diluted with diethyl ether (60 mL), and the organic solution was washed with water (30 mL), brine (30 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solution was filtered and concentrated *in vacuo*, the crude mixture was purified by column chromatography (SiO<sub>2</sub>, hexane : ethyl acetate = 3:1) to yield the product as yellow waxy solid. (R<sub>f</sub> = 0.45).

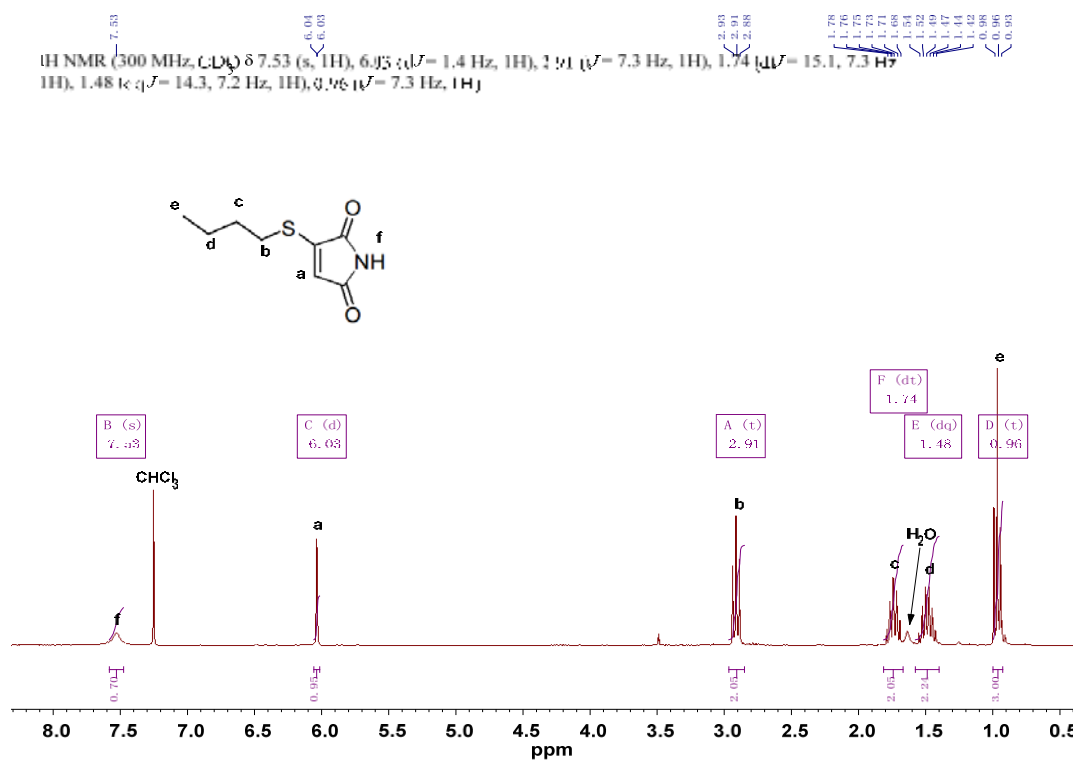


Fig. S2. <sup>1</sup>H NMR spectrum of 2-(butylthio)-maleimide in CDCl<sub>3</sub>.

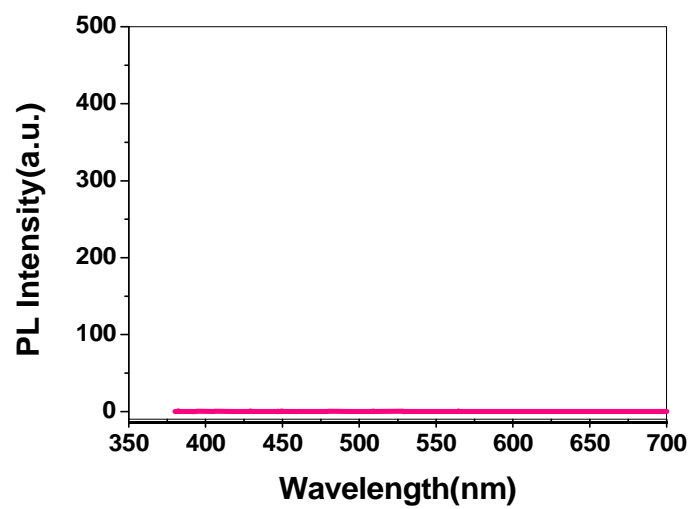
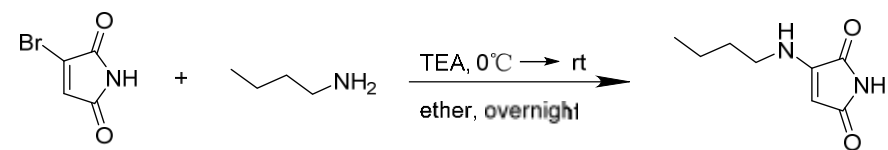


Fig. S3. Fluorescence spectrum of 2-(butylthio)-maleimide in  $\text{CDCl}_3$ .

## Synthesis of 2-(butylamino)-maleimide.



$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.04 (s, 1H), 5.35 (s, 1H), 4.81 (d,  $J=1.1$  Hz, 1H), 3.17 (d,  $J=13.1, 6.9$  Hz, 2H), 1.63 (d,  $J=19.6, 7.3$  Hz, 2H), 1.41 (q,  $J=14.3, 7.3$  Hz, 2H), 0.96 (t,  $J=7.3$  Hz, 3H)

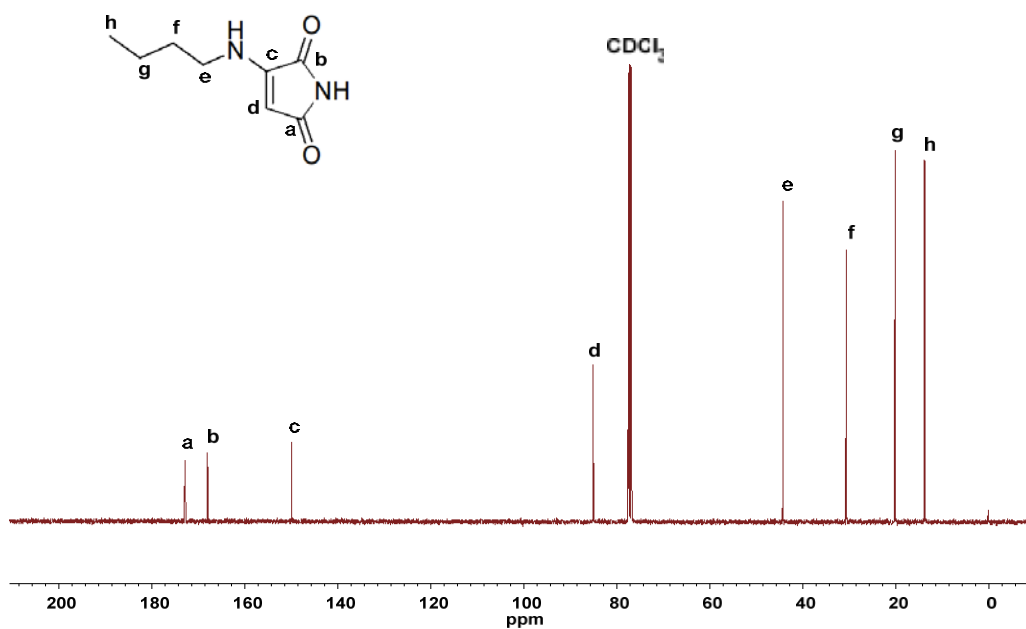
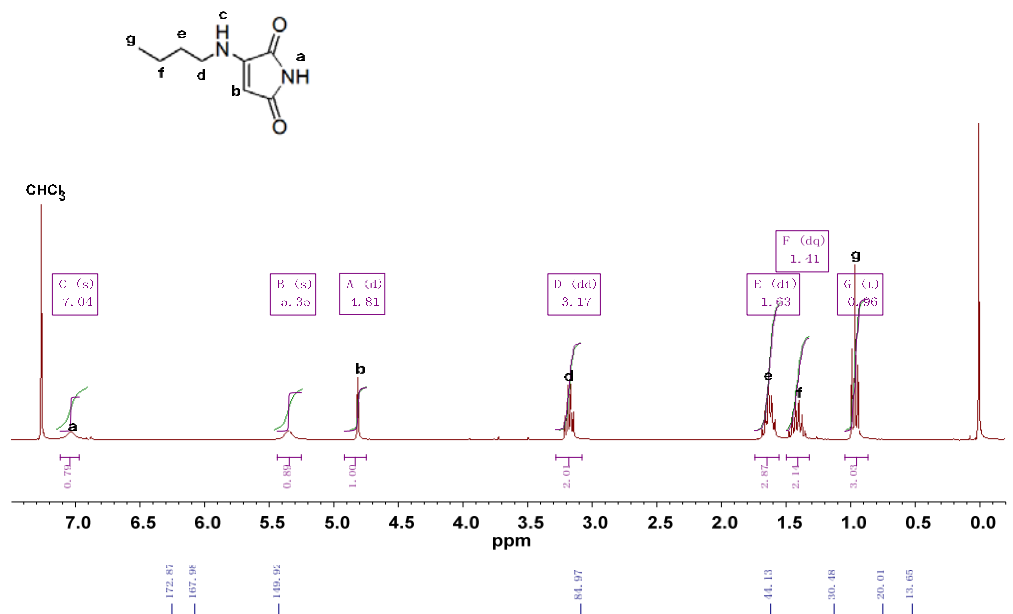


Fig. S4. (A)  $^1\text{H}$  and (B)  $^{13}\text{C}$  NMR spectra of 2-(butylamino)-maleimide in  $\text{CDCl}_3$ .

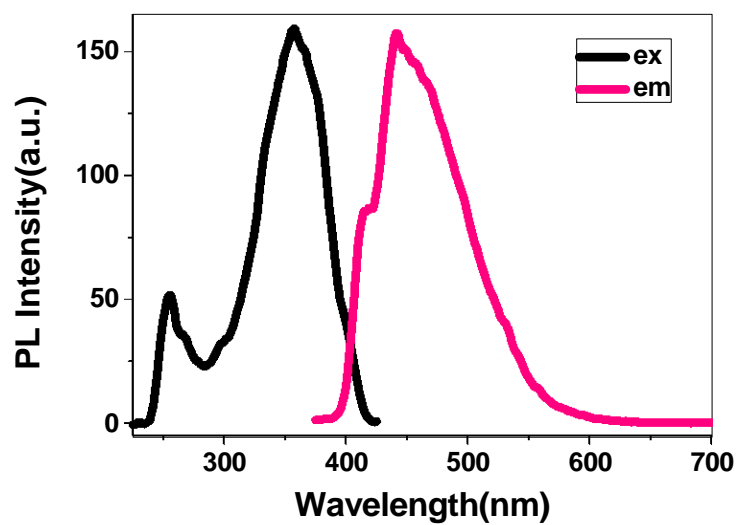
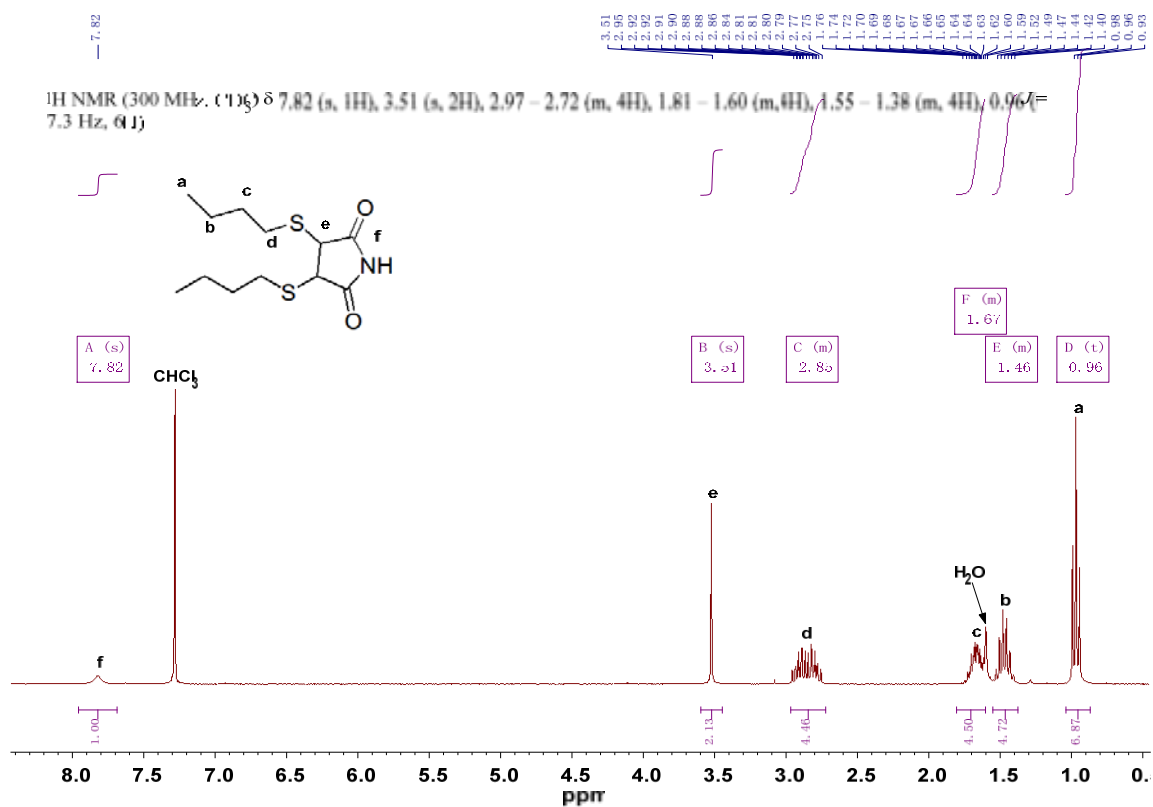


Fig. S5. Fluorescence spectrum of 2-(butylamino)-maleimide in  $\text{CDCl}_3$ .



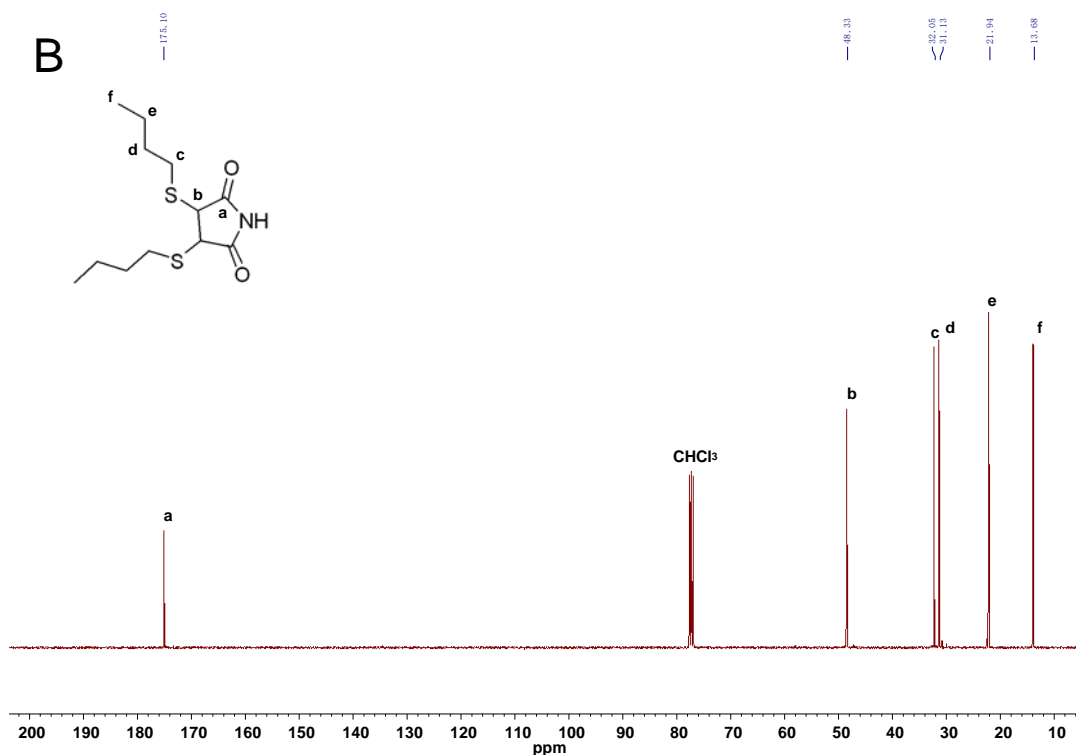


Fig. S6. (A) <sup>1</sup>H and (B) <sup>13</sup>C NMR spectra of 2,3-di(butylthio)-succinimide in CDCl<sub>3</sub>.

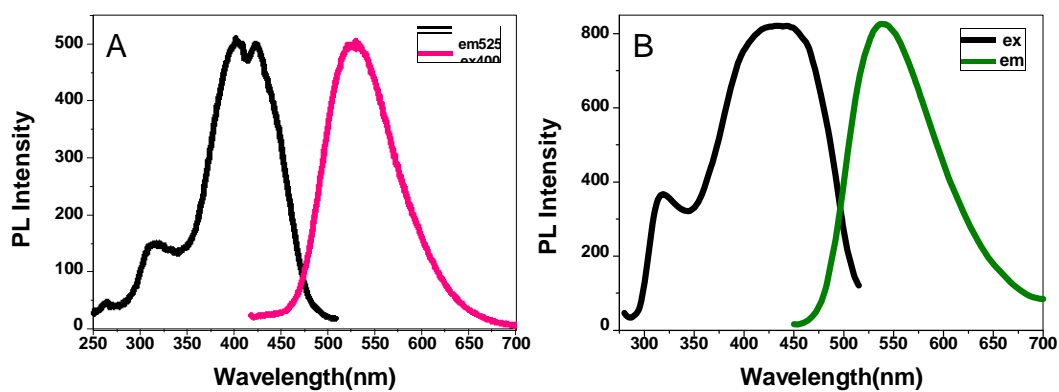
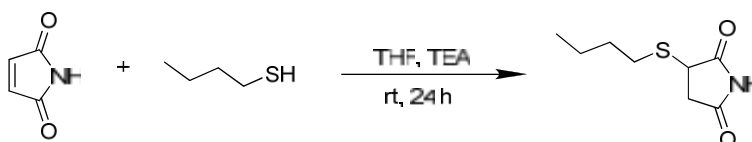


Fig. S7. Fluorescence spectra of 2,3-di(butylthio)-succinimide in chloroform (A) and bulk state (B).

### Synthesis of 2-(butylthio)-succinimide



Maleimide (262.1 mg, 2.70 mmol) was dissolved in 5 mL THF and purged with argon for 10 min, triethylamine (273.1 mg, 2.70 mmol) was added as a catalyst. Butanethiol (250.4 mg, 2.78 mmol) was added



in the presence of tributylphosphine (20  $\mu$ l). The solution was stirred at room temperature for 24 h. The solvent was removed and purified by flash chromatography ( $\text{SiO}_2$ , hexane: ethyl acetate = 3:2) to afford a pale yellow oil. ( $R_f = 0.35$ )

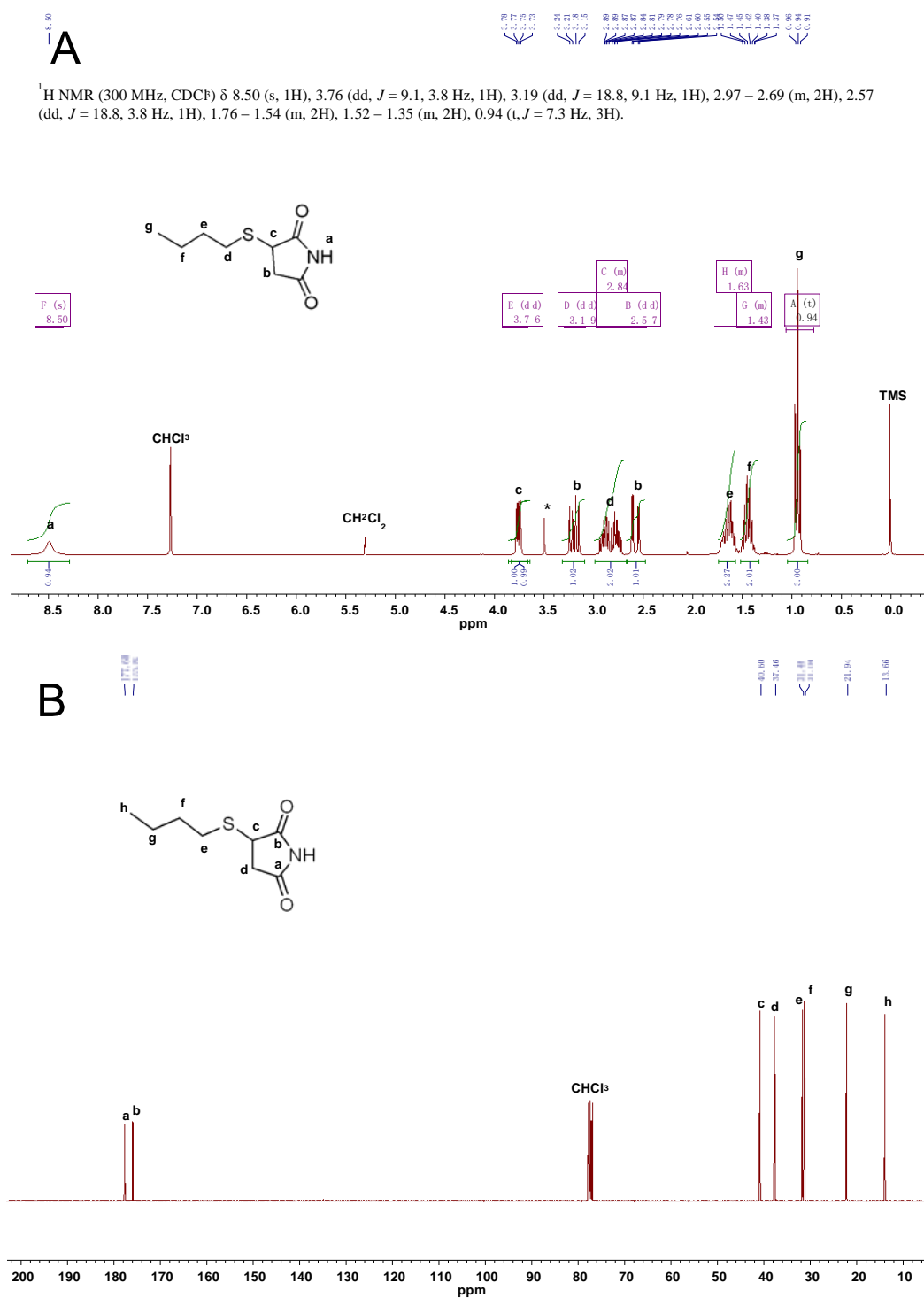


Fig. S8.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2-(butylthio)-succinimide in  $\text{CDCl}_3$ .

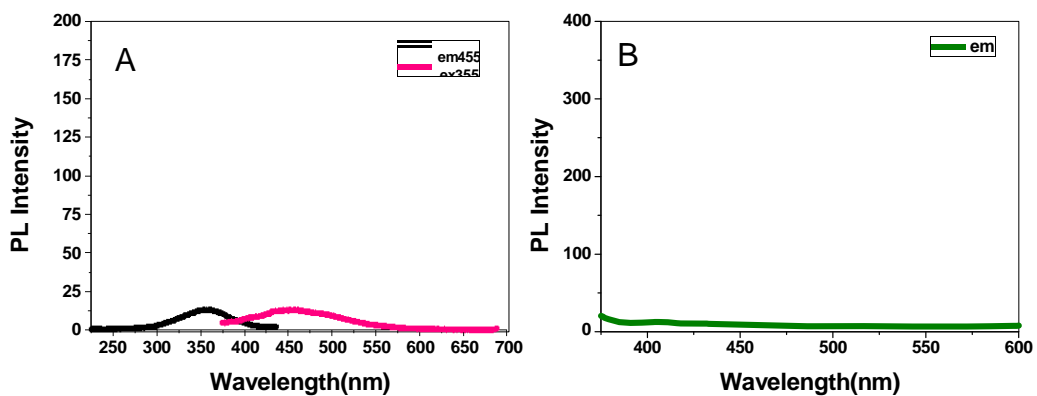
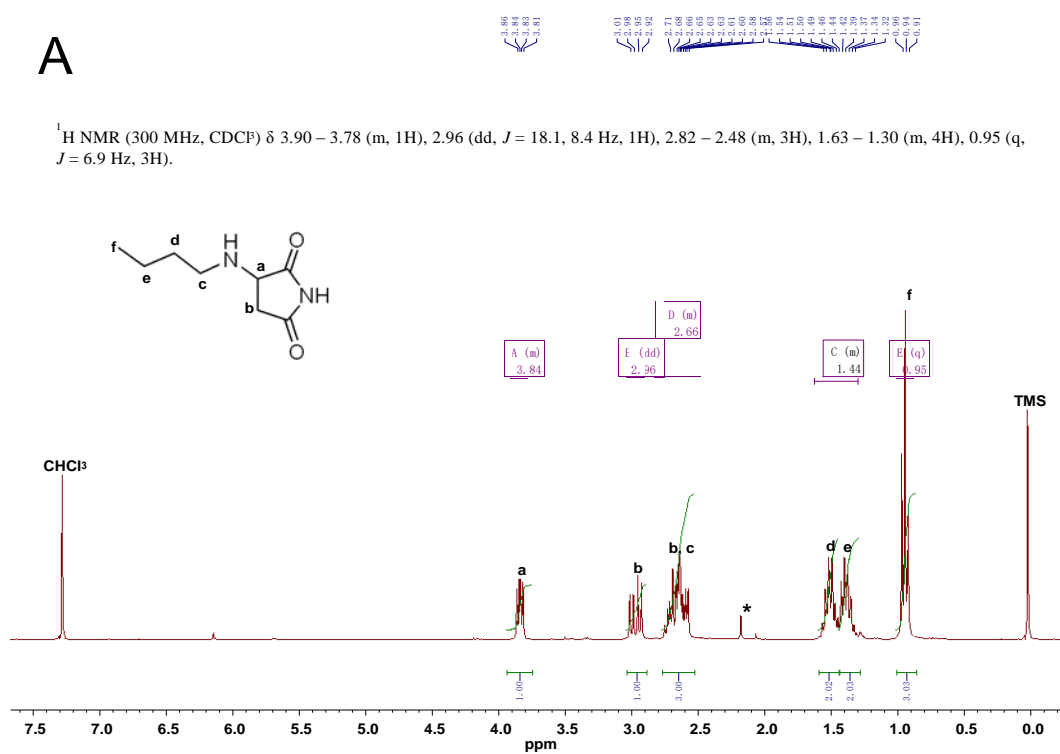


Fig. S9. Fluorescence spectra of 2-(butylthio)-succinimide in chloroform (A) and bulk state (B).



B

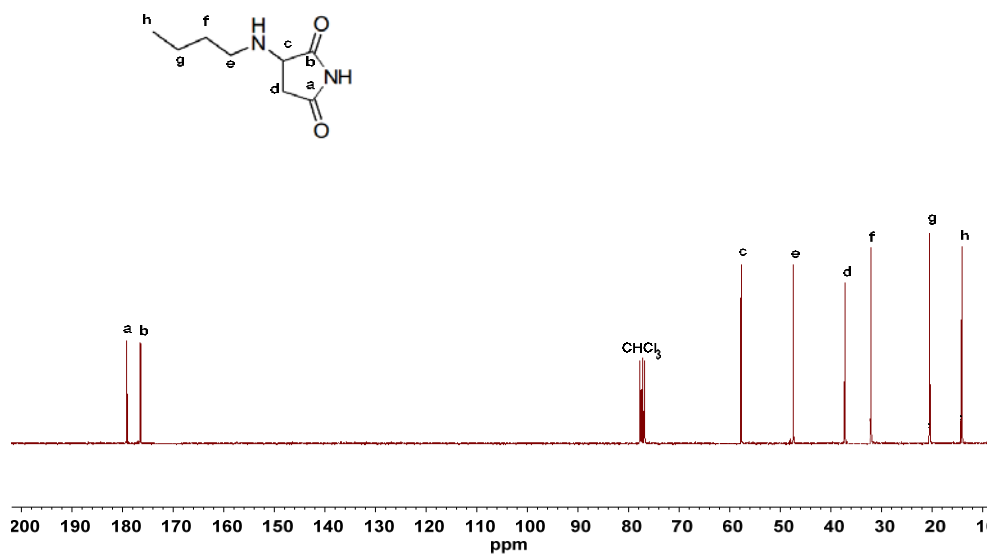


Fig. S10.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2-(butylamino)-succinimide in  $\text{CDCl}_3$ . \* assign to the solvent of ethyl acetate.

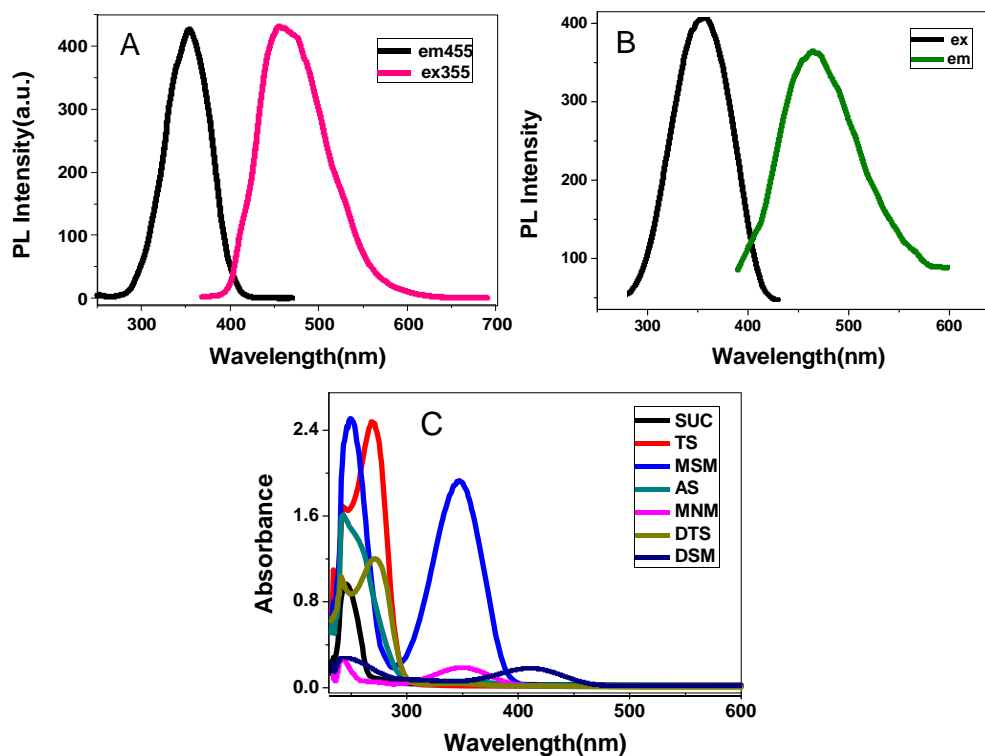


Fig. S11. Fluorescence spectra of 2-(butylamino)-succinimide in chloroform (A) and bulk state (B). (C) UV-vis spectra of thiol/amino succinimides and homologous maleimides. (Abbreviated instructions, SUC:

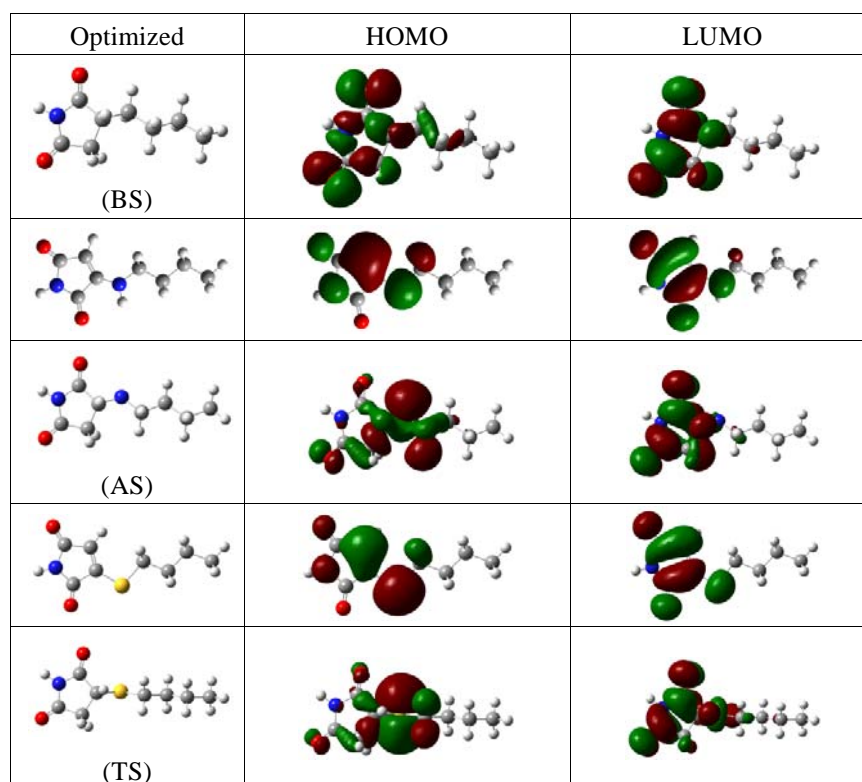
succinimide; TS: 2-thio-succinimide; MSM: 2-thio-maleimide; AS: 2-amino-succinimide; MNM: 2-amino-maleimide; DTS: 2,3-dithio-succinimide; DSM: 2,3-dithio-maleimide)

Table S1. Elemental Analysis Results of fluorescent dithio/amino-succinimides.

Sample	C %	H %	N %	S %
DTS (calculated)	52.33	7.69	5.09	23.28
DTS* (experiment)	52.48	7.72	5.10	23.41
AS (calculated)	56.45	8.29	16.46	-
AS (experiment)	56.31	8.32	16.49	-

\*DTS was recrystallized twice in hexane/methanol (20/1, v/v) before elemental analysis.

**Electronic structures.** The optimized structures and orbital distributions of HOMO and LUMO energy levels of nitrogen and thiol substituted succinimides and homologous maleimides were calculated utilizing density functional theory (DFT) at basis set of nonlocal density functional of B3LYP with 6-31G(d) with G03 program.



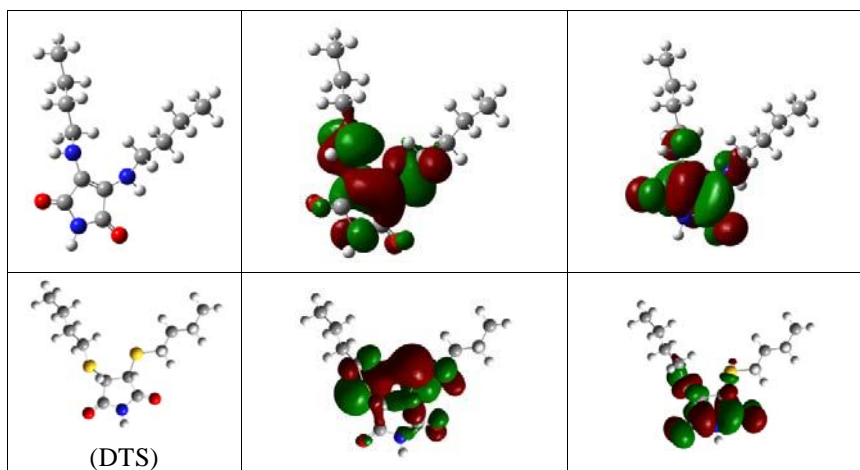


Fig. S12. Optimized structures, molecular orbital amplitude plots and energy levels of HOMOs and LUMOs of nitrogen and thiol substituted succinimides and homologous maleimides calculated by using B3LYP/6-31G(d) basis set with G03 program. (blue: nitrogen atom; yellow: sulfur atom; red: oxygen atom; grey: carbon atom; white: hydrogen atom.)

**Solvent effect.** The fluorescence of DTS and AS were characterized in diverse solvents with increasing polarities (hexane, toluene, dichloromethane, chloroform, THF, DMF, methanol and water), the subjected solutions were irradiated at same wavelength (405 nm for DTS, and 355 nm for AS).

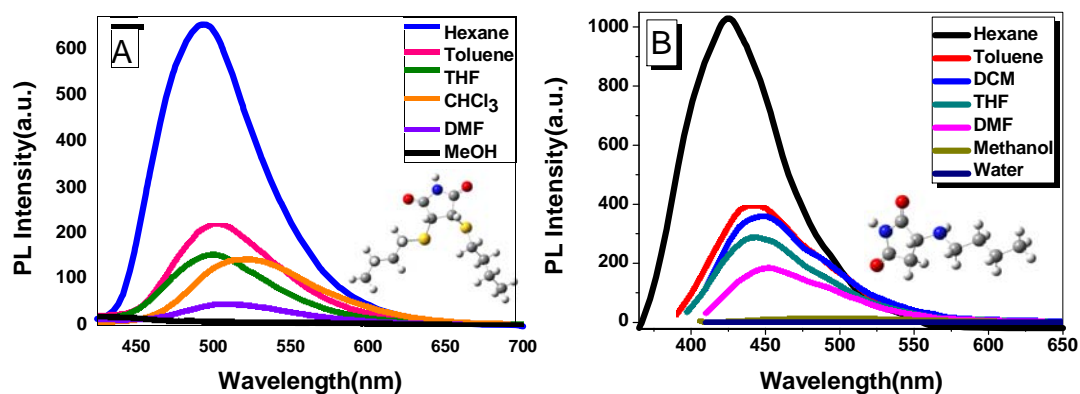


Fig. S13. Fluorescence spectra of DTS (A) and AS (B) in different solvents.

**Concentration effect.** Concentration effect on succinimides fluorescence were performed, DTS was excited at 405 nm. And AS had two absorptions at 330 nm and 405 nm, so the fluorescence signals irradiated at these two wavelengths were both collected.

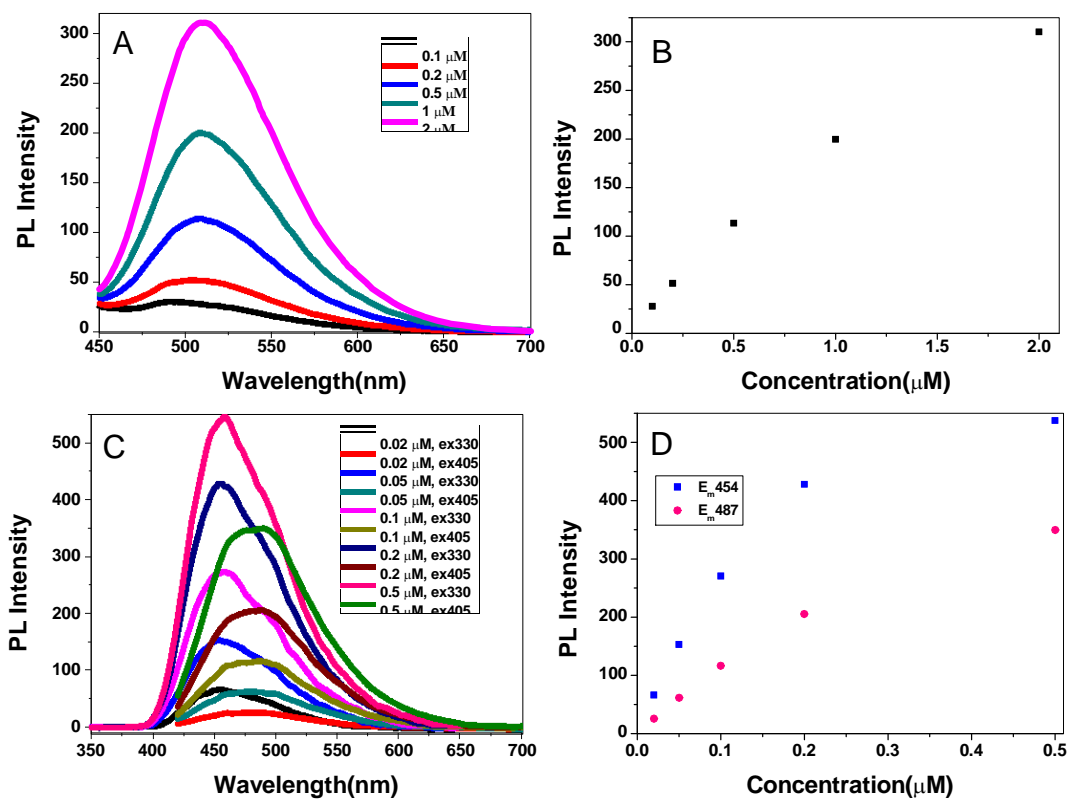


Fig. S14. Fluorescence spectra of DTS (A, B) and AS (C, D) solutions at varying concentrations.

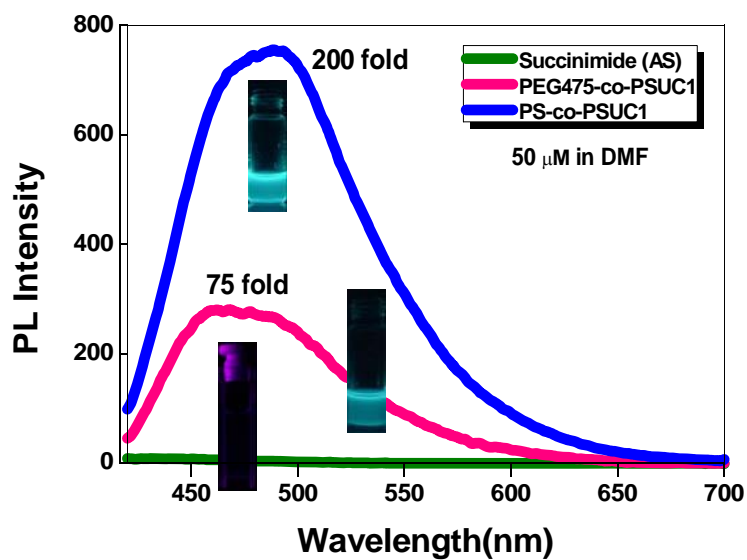


Fig. S15. Fluorescence enhancement of amino-succinimides after isolating by PEG475 (red) and PStyrene (blue) blocks.

### Copolymerization of 2, 3-(dibutylthio)-maleimide with Styrene.

Styrene (735.3 mg, 7.07 mmol), 2,3-(dibutylthio)-maleimide (55.2 mg, 0.202 mmol) and AIBN (11.9 mg, 0.0727 mmol) were dissolved in 1.0 mL THF purged with argon atmosphere, and placed to preheated oil at 80°C for 20 h. The mixture was diluted with 2 mL THF and precipitated into methanol twice and dried vacuum for 2 h to obtain slight yellow powders.

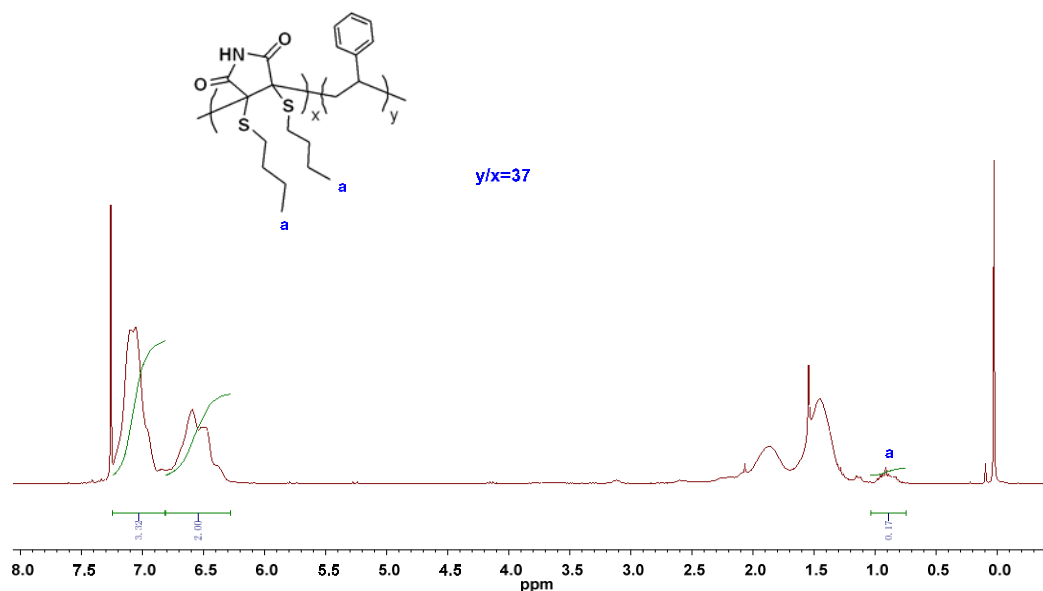


Fig. S16.  $^1\text{H}$  NMR spectrum of PS-co-PSUC3 in  $\text{CDCl}_3$ .

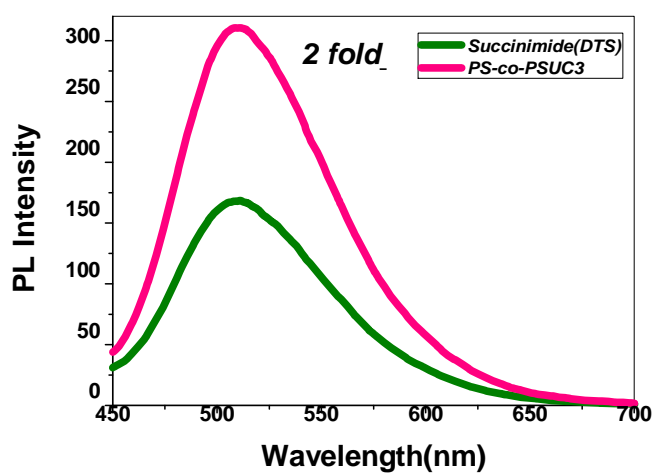


Fig. S17. Fluorescence enhancement of DTS after copolymerizing with Styrene (red).

**Quantum yields of succinimides and corresponding polymers.** Quinine sulfate was chosen as standards for fluorescence quantum yield measurements. Usually the solutions with optical densities should be controlled

between 0.1 and 0.01. However, because of the weak additional absorbance of DTS and AS at excitation wavelengths, the optical density was controlled between 1.50 and 2.0. The quantum yields of polymers are calculated using:

$$Q = Q_R \frac{I}{I_R} \frac{OD_R n^2}{OD n_R^2}$$

Where Q is the quantum yield, I is the integrated intensity, n is the refractive index, OD is the optical density. The subscript R refers to the reference chromophore of known quantum yield. The quantum yield of quinine sulfate in 0.1 M H<sub>2</sub>SO<sub>4</sub> at 22 °C is 0.58 (350 nm excitation).

*Table S2.* Quantum yields and molar absorptivities of succinimides, homologous maleimides and corresponding copolymers in DMF and hexane.

Sample	Quantum yields in DMF	Quantum yields in CHCl <sub>3</sub>	Quantum yields in hexane	Molar absorptivity (in CHCl <sub>3</sub> , M <sup>-1</sup> cm <sup>-1</sup> )
2,3-di(butylthio)-succinimide (DTS)	0.01	0.03	0.12	21 (346 nm), 662 (271 nm)
2-(butylthio)-succinimide (TS)	<0.001	<0.005	<0.005	-
2-(butylamino)-succinimide (AS)	0.44 <sup>a</sup>	0.47 <sup>a</sup>	0.56 <sup>a</sup>	171 (243 nm)
2,3-di(butylthio)-maleimide	0.034	0.11	0.48	9414 (411 nm), 15415 (242 nm)
2-(butylamino)-maleimide	0.38	0.47	0.64	9411 (350 nm), 5988 (241 nm)
PEG475-co-PSUC1	0.29	0.32	- <sup>b</sup>	-
PS-co-PSUC1	0.38	0.41	- <sup>b</sup>	-
PS-co-PSUC3	0.006	0.008	- <sup>b</sup>	-

<sup>a</sup> the absorbance of samples were very low, leading to apparently high quantum yields, but DTS showed much stronger fluorescence than AS under hand-held UV lamp (365 nm).

<sup>b</sup> samples didn't dissolve well in solvents.

## References

1. J. J. Yan, D. Wang, D. C. Wu and Y. Z. You, *Chem. Commun.* 2013, **49**, 6057-6059.



2. L. M. Tedaldi, M. E. B. Smith, R. I. Nathani and J. R. Baker, *Chem. Commun.* 2009, **43**, 6583-6585.

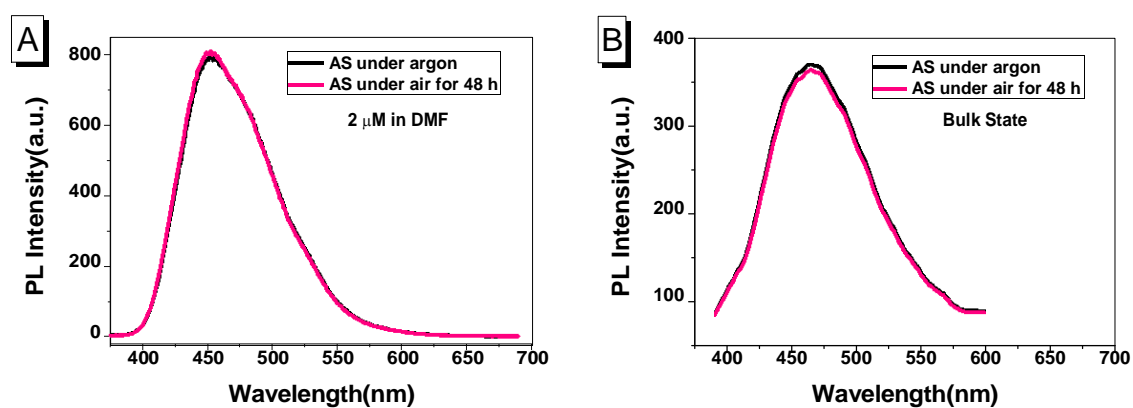


Fig. S18. Fluorescence spectra of AS under argon and air, both in solution (A) and at bulk state (B).

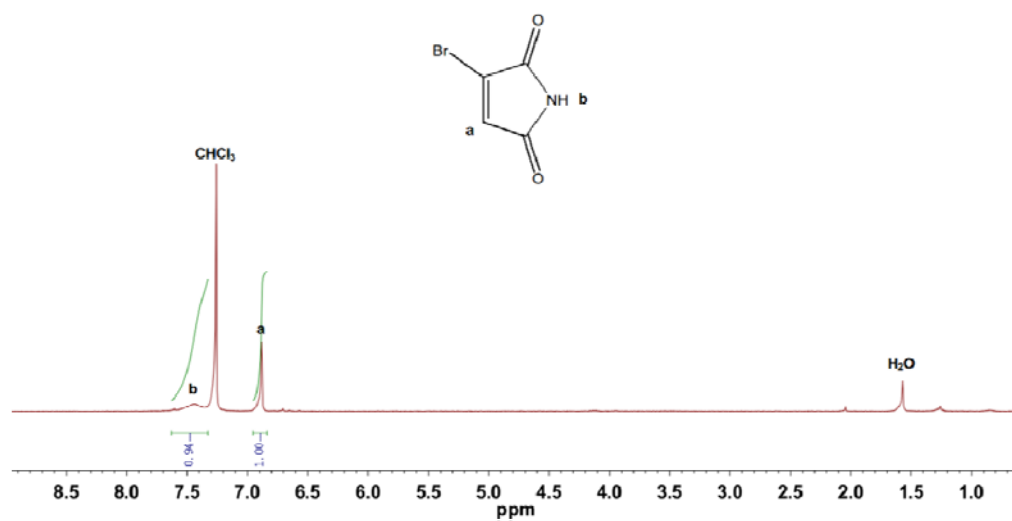


Fig. S19 <sup>1</sup>H NMR spectrum of bromomaleimide in CDCl<sub>3</sub>.