

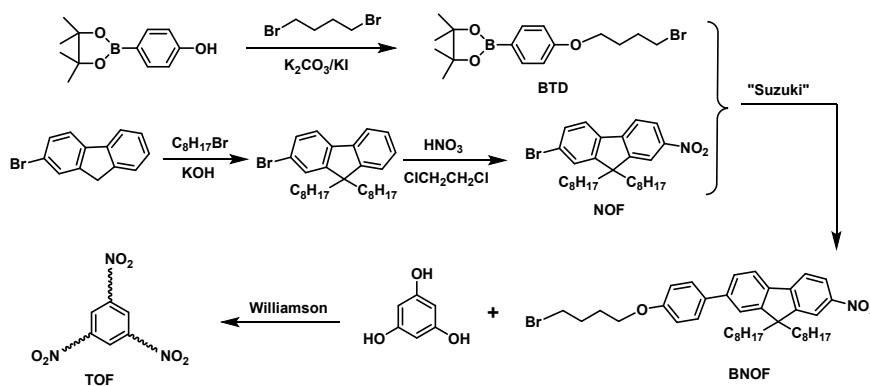
## Supporting Information

# Synthesis and Characterization of Visible–Light–Activated Azo Hyperbranched Polymers

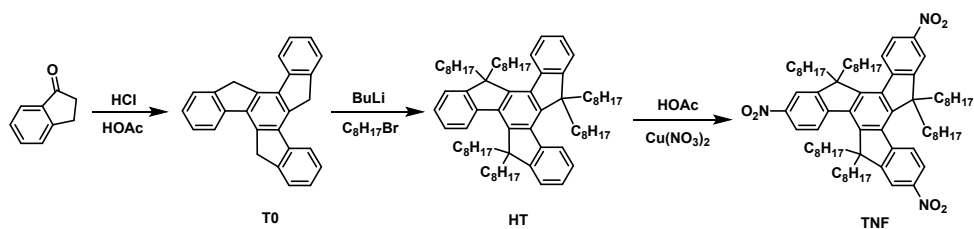
*Laibing Wang, Yang Chen, Lu Yin, Shuangshuang Zhang, Nianchen Zhou, Wei Zhang,\* and  
Xiulin Zhu*

State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Jiangsu  
Key Laboratory of Advanced Functional Polymer Design and Application, Suzhou Key  
Laboratory of Macromolecular Design and Precision Synthesis, College of Chemistry, Chemical  
Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China

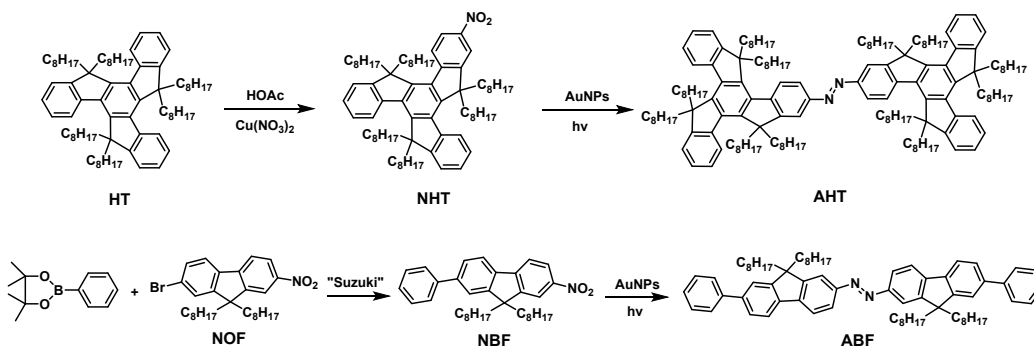
Email: weizhang@suda.edu.cn



**Scheme S1** Synthetic routes of trinitro-functionalized monomers (TOF).



**Scheme S2** Synthetic routes of trinitro-functionalized monomers (TNF).



**Scheme S3** Synthetic routes of Azo compounds AHT and ABF.

### Synthesis of (*E*)-1,2-bis(5,5,10,10,15,15-hexaoctyl-10,15-dihydro-5*H*-diindeno[1,2-*a*:1',2'-*c*]fluoren-2-yl)diazene (AHT)

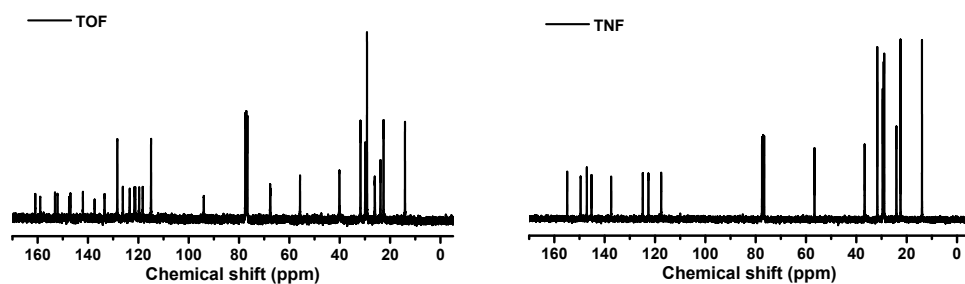
The synthetic method of AHT is similar to the method described as our previous reported.<sup>1</sup> Yield, 80%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ (TMS, ppm): 8.46-8.63, 8.28-8.44, 8.11, 8.04, 7.32-7.55, (22H, Ar-*H*), 2.82-3.20 (12H, CH<sub>2</sub>CCH<sub>2</sub>), 1.95-2.36 (12H, CH<sub>2</sub>CCH<sub>2</sub>), 0.79-1.19 (120H, CH<sub>2</sub>), 0.73 (36H, CH<sub>2</sub>CH<sub>3</sub>), 0.54 (24H, CH<sub>2</sub>CH<sub>3</sub>). MALDI-TOF-MS: *m/z* calcd for C<sub>150</sub>H<sub>226</sub>N<sub>2</sub> [M]<sup>+</sup>: 2055.77, found 2055.77.

### Synthesis of (*E*)-1,2-bis(9,9-dioctyl-7-phenyl-9*H*-fluoren-2-yl)diazene (ABF)

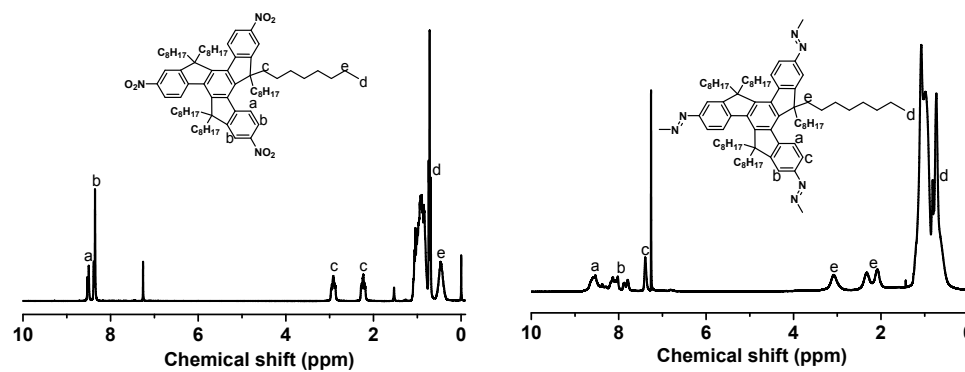
The synthetic method of ABF is similar to the method described as AHT. Yield, 90%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ (TMS, ppm): 8.02, 7.98, 7.87, 7.84, 7.69, 7.63, 7.59, 7.49, 7.38 (22H, Ar-

*H*), 1.97-2.22 (8H,  $CH_2CCH_2$ ), 0.93-1.23 (40H,  $CH_2$ ), 0.79 (12H,  $CH_2CH_3$ ), 0.71 (8H,  $CH_2CH_3$ ).

MALDI-TOF-MS:  $m/z$  calcd for  $C_{70}H_{90}N_2 [M]^+$ : 958.71, found 958.72.

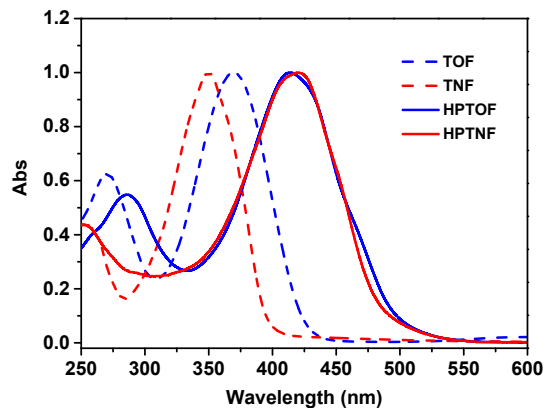


**Fig. S1**  $^{13}C$  NMR spectra of monomer TOF (left) and TNF (right) in  $CDCl_3$ .

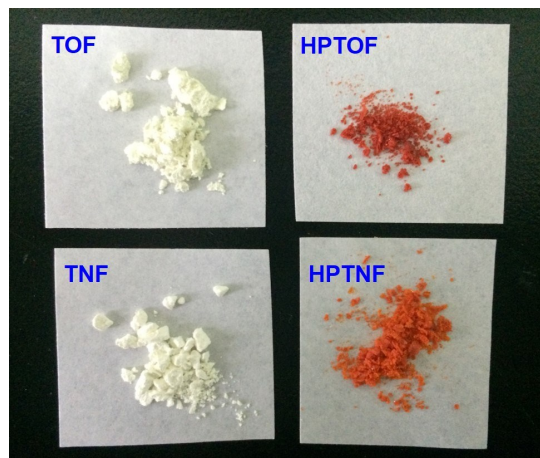


**Fig. S2**  $^1H$  NMR spectra of monomer TNF (left) and azo hyperbranched polymer HPTNF

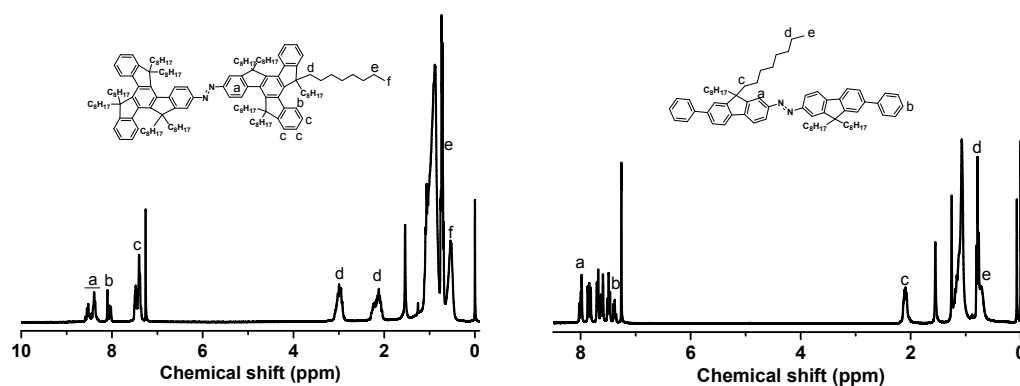
( $M_{w,TD-GPC} = 144900$  g/mol, PDI = 2.81) (right) in  $CDCl_3$ .



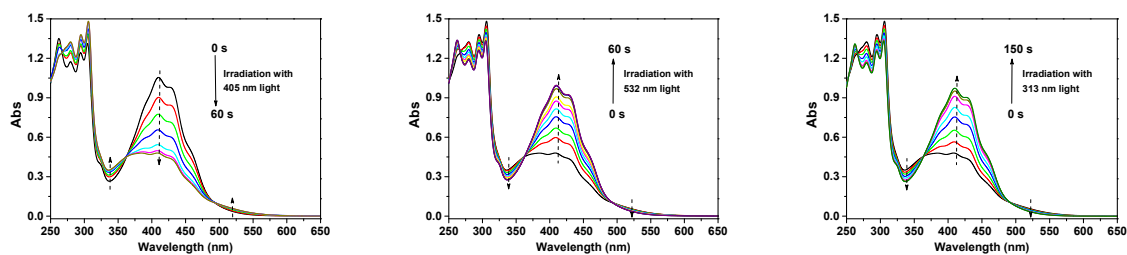
**Fig. S3** The UV-vis absorption spectra of TOF, TNF, HPTOF ( $M_{w,TD-GPC} = 125700$  g/mol, PDI = 2.62) and HPTNF ( $M_{w,TD-GPC} = 144900$  g/mol, PDI = 2.81). All traces were normalized to height.



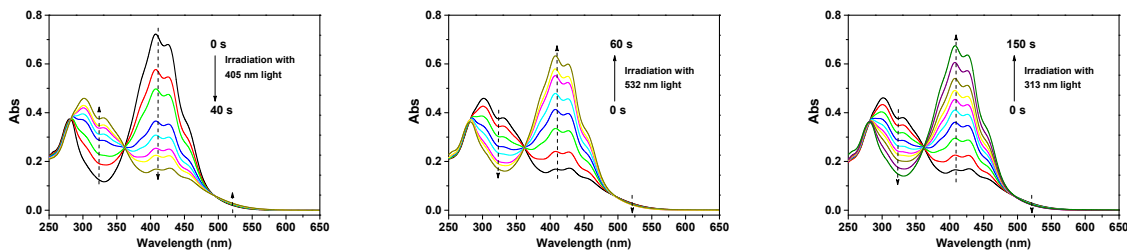
**Figure S4.** The obvious color change before and after polymerization.



**Fig. S5**  $^1\text{H}$  NMR spectra of monomer AHT (left) and ABF (right) in  $\text{CDCl}_3$ .



**Fig. S6** Time evolution of the UV-vis absorption spectra of ATH upon 405/532/313 nm light irradiation with different time interval in tetrahydrofuran. The concentration of solutions are both  $1 \times 10^{-2}$  mg/mL for ATH.



**Fig. S7** Time evolution of the UV-vis absorption spectra of ABF upon 405/532/313 nm light irradiation with different time interval in tetrahydrofuran. The concentration of solutions are both  $1 \times 10^{-2}$  mg/mL for ABF.

1. L. B. Wang, X. Q. Pan, Y. Zhao, Y. Chen, W. Zhang, Y. F. Tu, Z. B. Zhang, J. Zhu, N. C. Zhou and X. L. Zhu, *Macromolecules*, 2015, **48**, 1289.