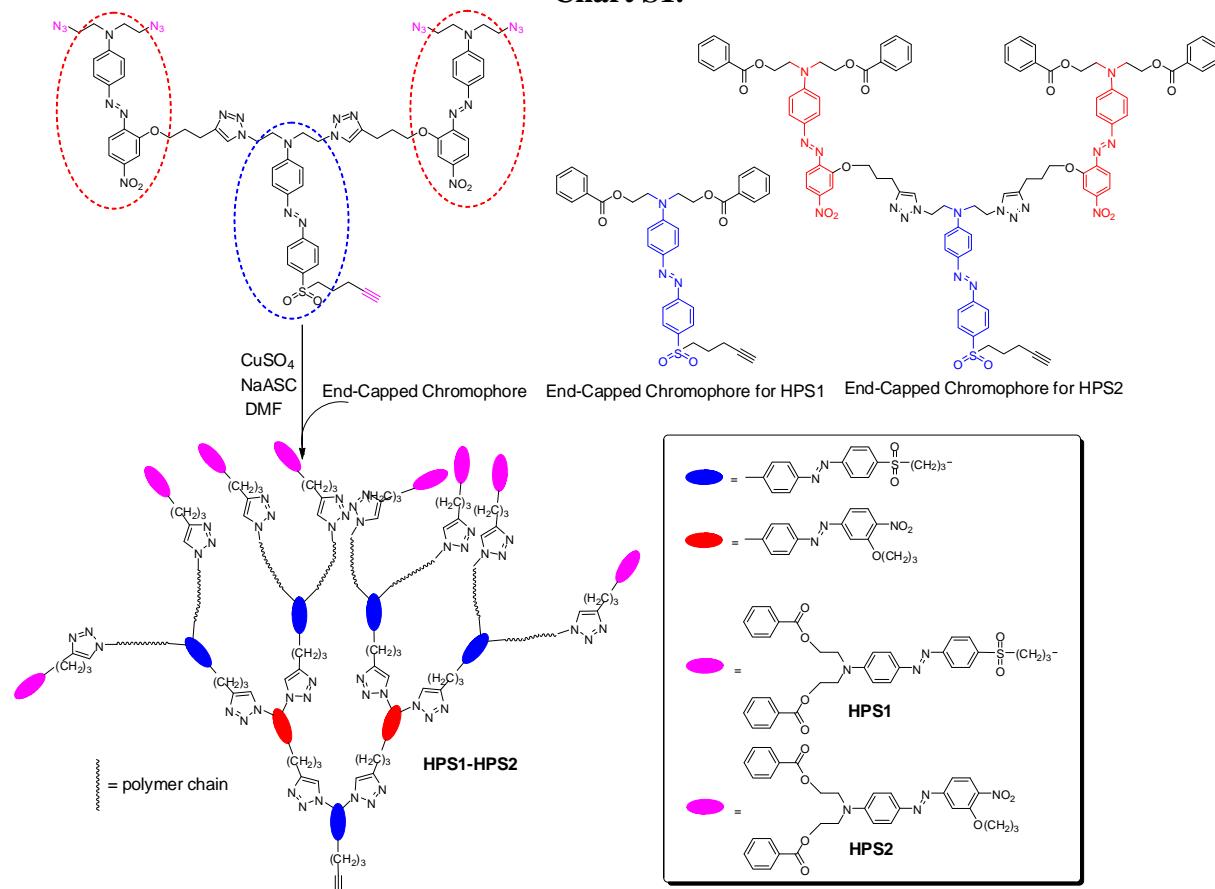


## Electronic Supplementary Information:

### New Second-Order Nonlinear Optical (NLO) Polymers Containing Isolation Chromophore Derived from One-Pot “A<sub>2</sub>+B<sub>4</sub>” Approach via Suzuki Coupling Reaction

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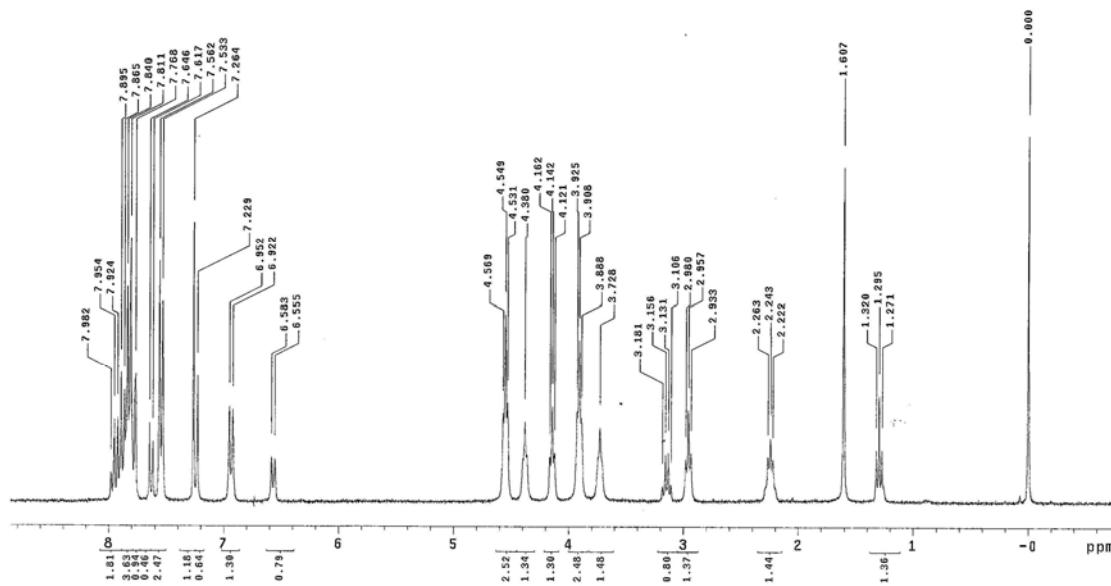
Chart S1.



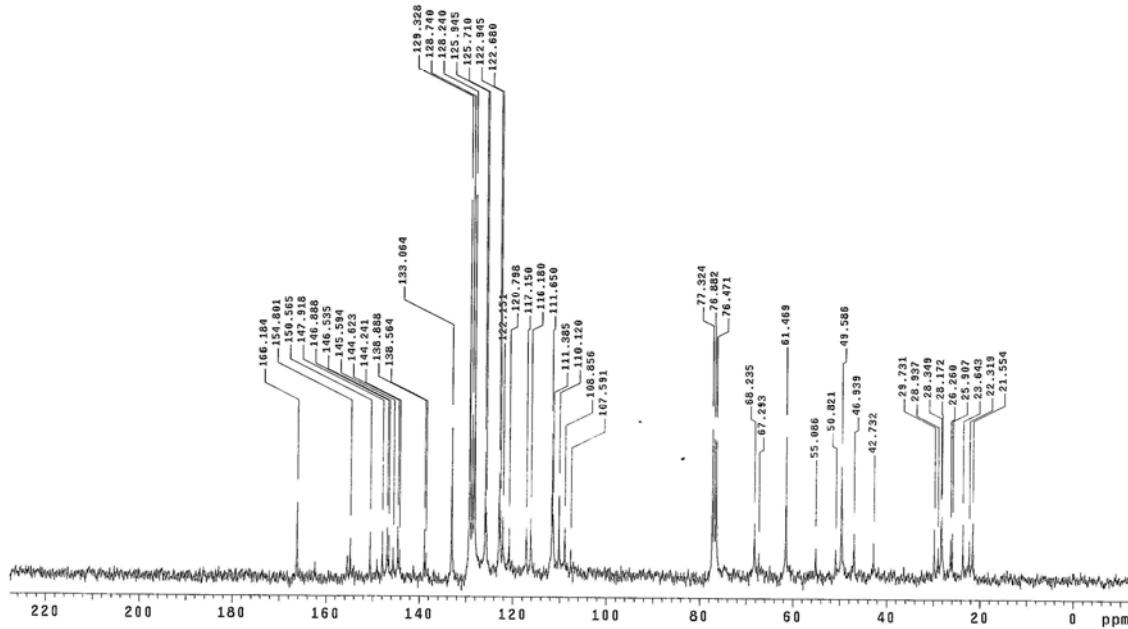
**Table S1. Characterization data of hyperbranched polymers.**

no.	$M_w^{[a]}$ ( $\times 10^5$ )	$M_w/M_n^{[a]}$	$T_g^{[b]}$ (°C)	$T_d^{[c]}$ (°C)	$T_e^{[d]}$ (°C)	$l_s^{[e]}$ (μm)	$d_{33}^{[f]}$ (pm/V)	$d_{33(\infty)}^{[g]}$ (pm/V)	$\Phi^{[h]}$	$\lambda_{\max}^{[i]}$ (nm)
<b>HPS1</b>	1.25	2.06	97	243	120	0.22	117.6	24.8	0.22	458
<b>HPS2</b>	1.79	2.42	100	284	125	0.25	167.4	31.5	0.26	466

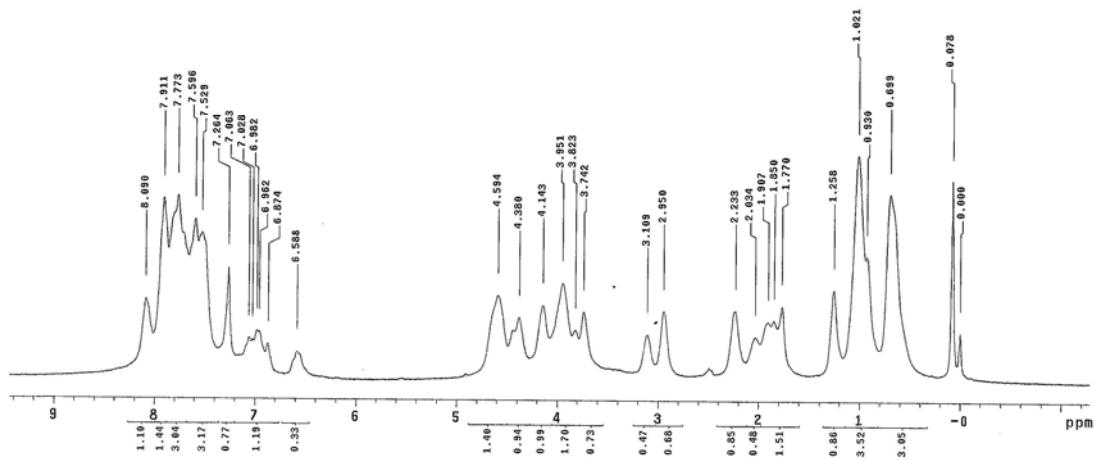
[a] Determined by GPC in DMF on the basis of a polystyrene calibration. [b] Glass transition temperature ( $T_g$ ) of polymers detected by the DSC analyses under argon at a heating rate of 10 °C/min. [c] the 5 % weight loss temperature of polymers detected by the TGA analyses under nitrogen at a heating rate of 10 °C/min. [d] the best poling temperature. [e] Film thickness. [f] Second harmonic generation (SHG) coefficient. [g] The nonresonant  $d_{33}$  values calculated by using the approximate two-level model. h Order parameter  $\Phi = 1 - A_1/A_0$ ,  $A_1$  and  $A_0$  are the absorbance of the polymer film after and before the corona poling, respectively. [i] The maximum absorption wavelength of polymer films.



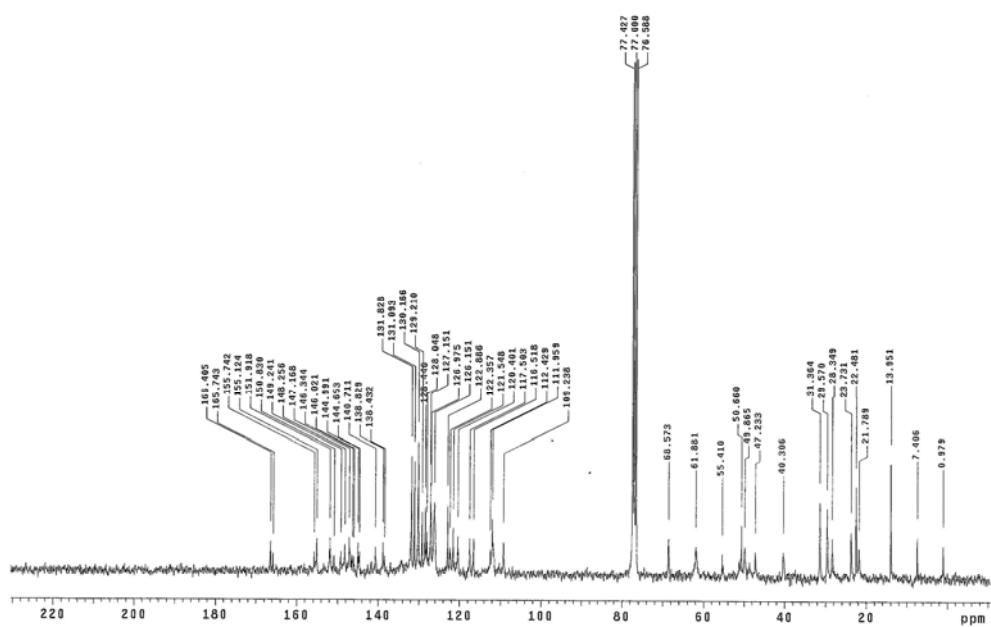
**Figure S1.** <sup>1</sup>H NMR spectrum of A<sub>4</sub>-type monomer C1 in chloroform-d.



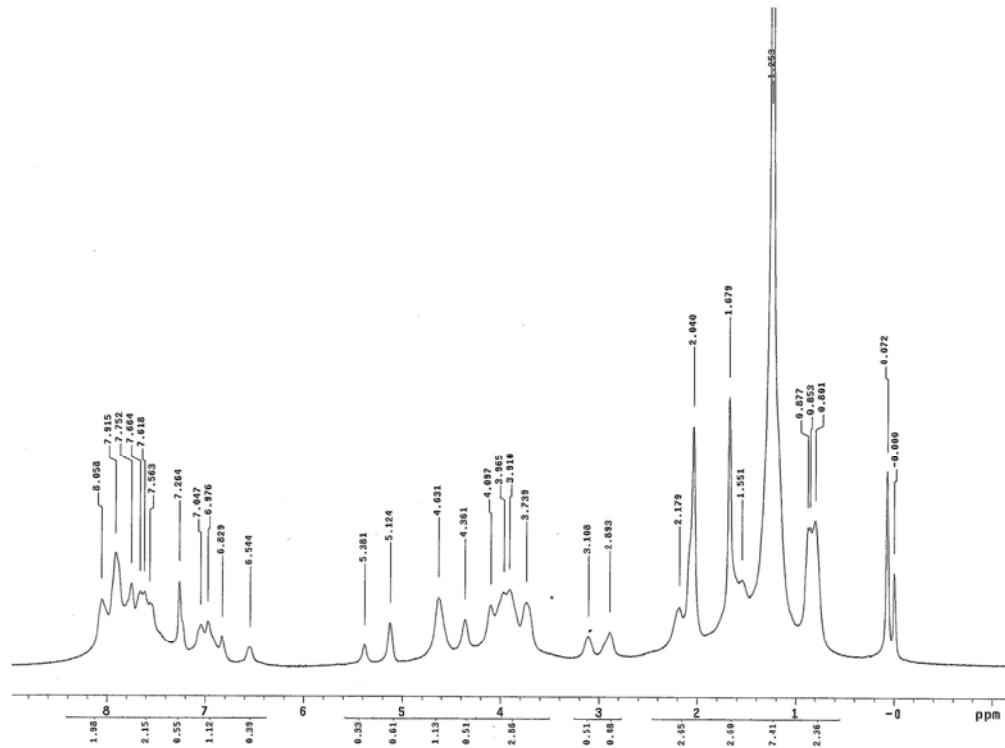
**Figure S2.** <sup>13</sup>C NMR spectrum of A<sub>4</sub>-type monomer C1 in chloroform-d.



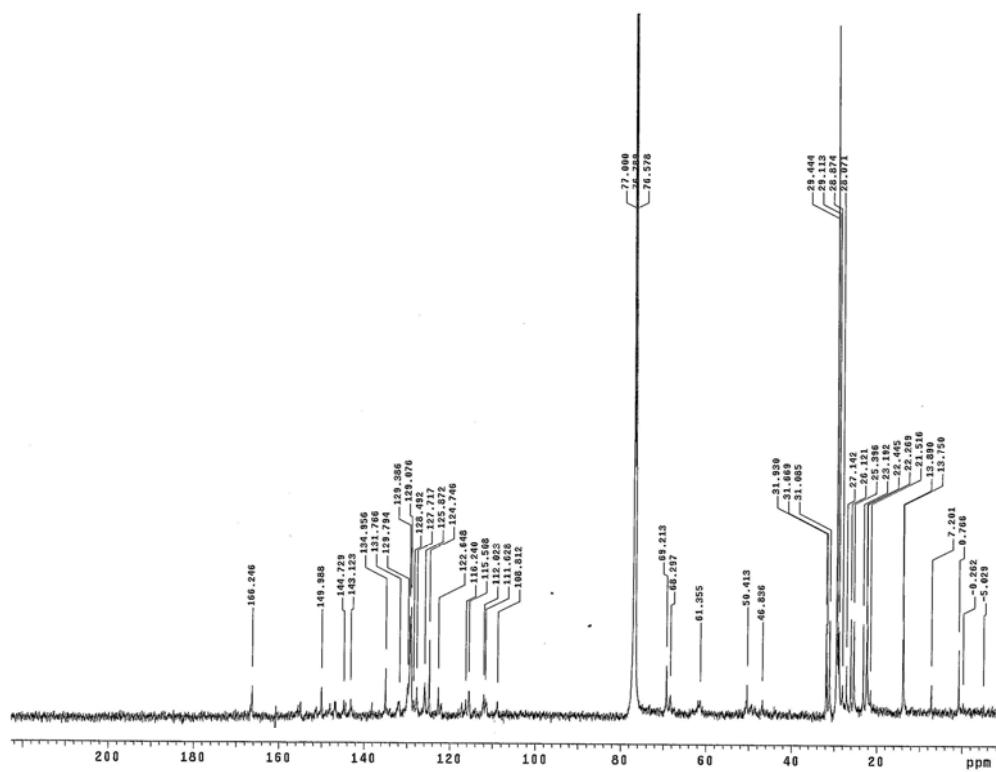
**Figure S3.** <sup>1</sup>H NMR spectrum of hyperbranched polymer HP1 in chloroform-d.



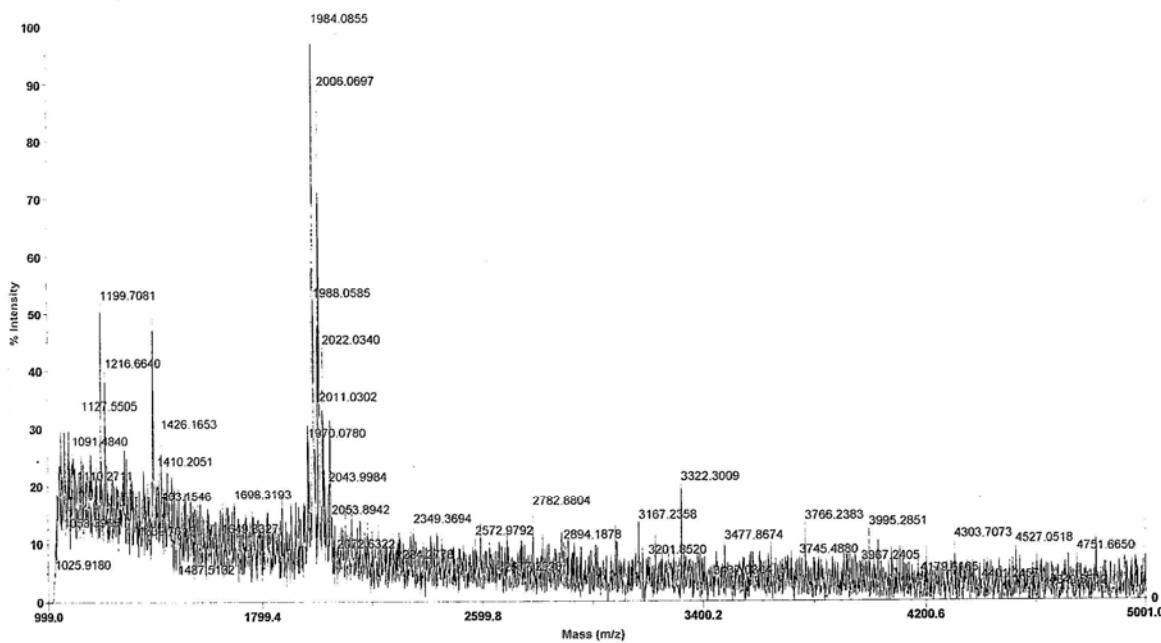
**Figure S4.** <sup>13</sup>C NMR spectrum of hyperbranched polymer **HP1** in chloroform-*d*.



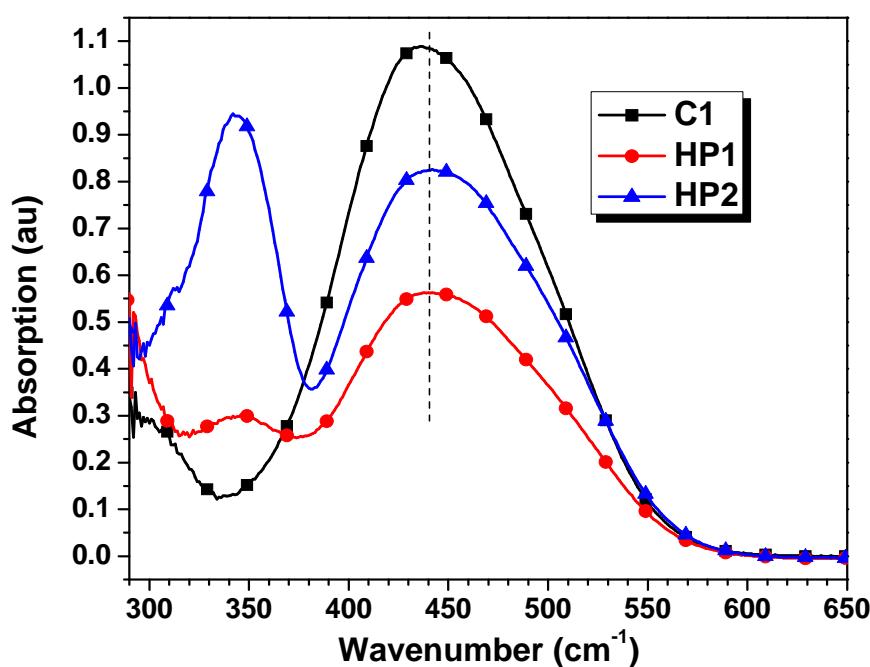
**Figure S5.** <sup>1</sup>H NMR spectrum of hyperbranched polymer **HP2** in chloroform-*d*.



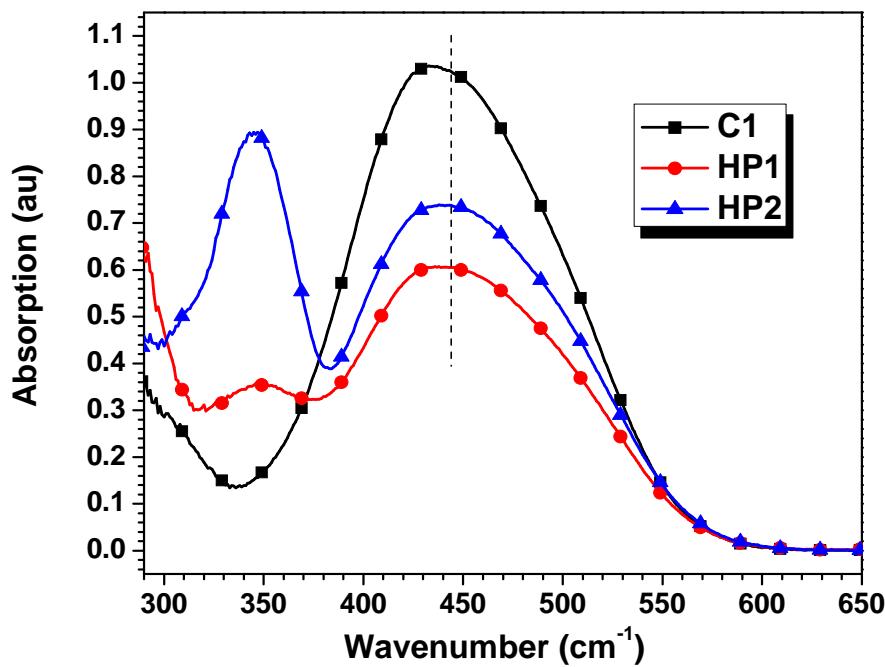
**Figure S6.** <sup>13</sup>C NMR spectrum of hyperbranched polymer **HP2** in chloroform-*d*.  
Voyager Spec #1 [EF = 1984.1, 1624]



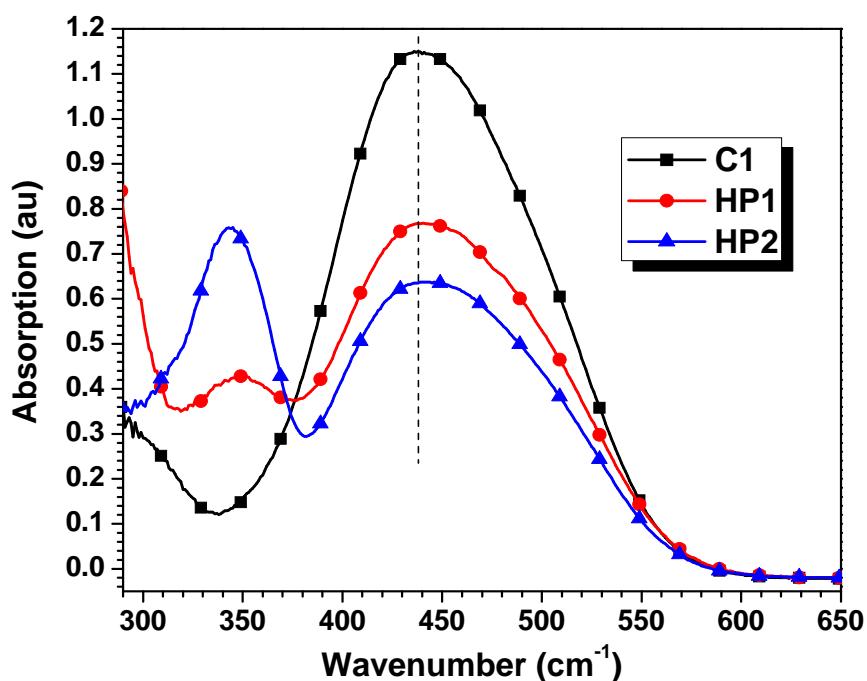
**Figure S7.** MALDI-TOF spectrum of A<sub>4</sub>-type monomer **C1**.



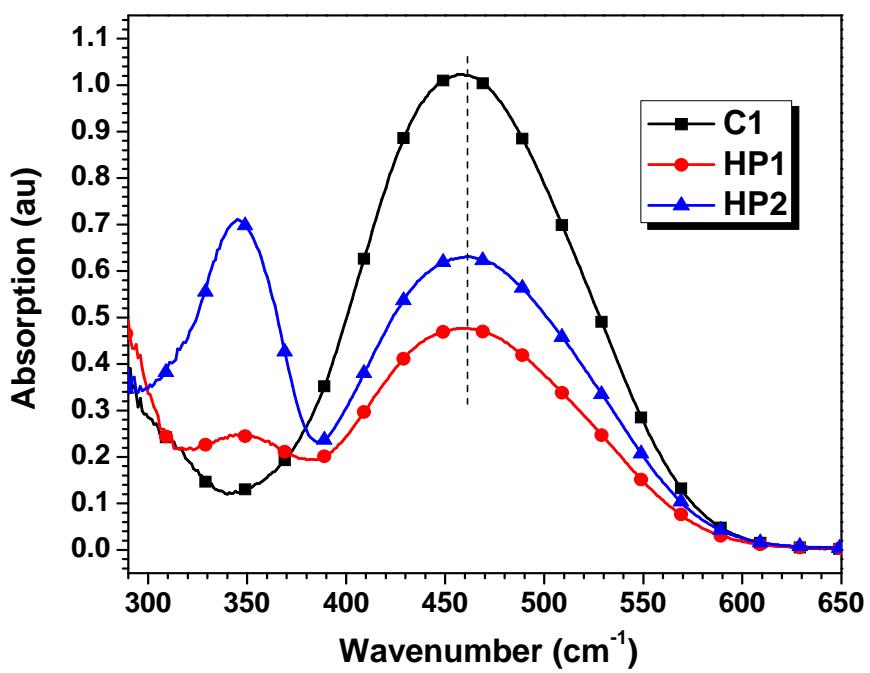
**Figure S8.** UV-Vis spectra of hyperbranched polymers **HP1-HP2** and their corresponding monomer **C1** in 1, 4-Dioxane (0.02 mg/mL).



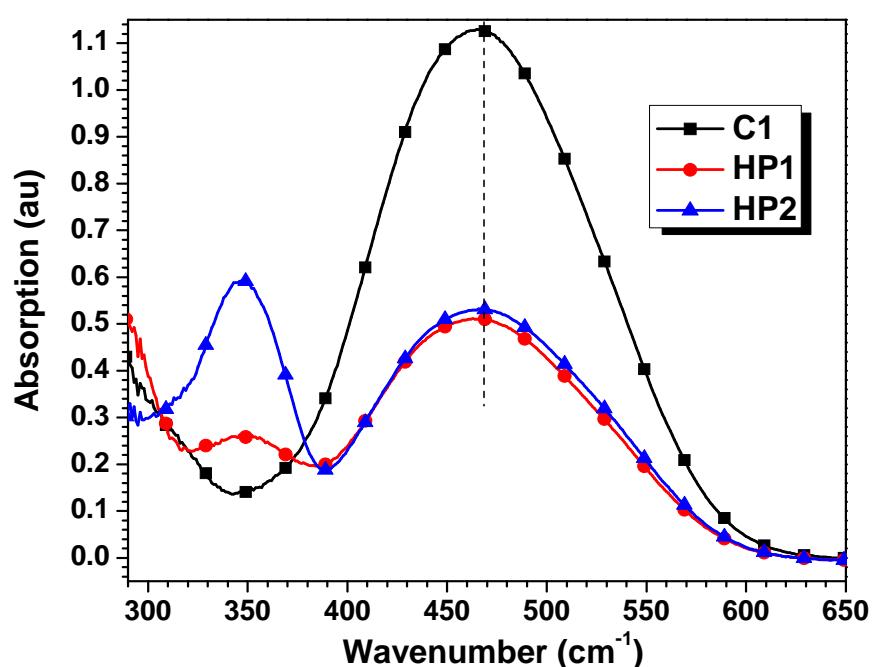
**Figure S9.** UV-Vis spectra of hyperbranched polymers **HP1-HP2** and their corresponding monomer **C1** in chloroform (0.02 mg/mL).



**Figure S10.** UV-Vis spectra of hyperbranched polymers **HP1-HP2** and their corresponding monomer **C1** in dichloromethane (0.02 mg/mL).



**Figure S11.** UV-Vis spectra of hyperbranched polymers **HP1-HP2** and their corresponding monomer **C1** in DMF (0.02 mg/mL).



**Figure S12.** UV-Vis spectra of hyperbranched polymers **HP1-HP2** and their corresponding monomer **C1** in DMSO (0.02 mg/mL).