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## **Electronic Supplementary Information**

# Janus second-order Nonlinear Optical Dendrimers: the Controllable Molecular Topology, and the corresponding Largely Enhanced Performance

Runli Tang,<sup>†a</sup> Shengmin Zhou,<sup>†a</sup> Ziyao Cheng, <sup>a</sup> Gui Yu, <sup>b</sup> Qian Peng, <sup>b</sup> Huiyi Zeng, <sup>c</sup> Guocong Guo, <sup>c</sup> Qianqian Li<sup>a</sup> and Zhen Li <sup>\*a</sup>

<sup>a</sup> Department of Chemistry, Wuhan University, Wuhan 430072, P. R. China.

<sup>b</sup> Institute of Chemistry, the Chinese Academy of Sciences, Beijing 100080, P. R. China.

<sup>c</sup> Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences, Fuzhou 350002, P. R. China.

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## **1** Dendrimers in previous study

Tree-like NLO dendrimers **G1-G3** were designed and prepared at the very beginning, demonstrating that the tested NLO effects increased accompanying with the increasing loading density of the chromophore moieties. It indicated that the frequently observed asymptotic dependence of electrooptic activity on the chromophore number density may be overcome through rational design.<sup>1a</sup> Then higher generation dendrimers **G4-G5** were prepared, excitingly, the measured NLO coefficient values increased from 123 (**G3**) to 177 (**G4**) to 193 pm/V(**G5**). The tested NLO effect (193 pm/V) was the highest value reported for the polymers containing simple azo chromophore moieties at that time.<sup>1b</sup> The synthetic route to **G5** was somewhat tedious, and the dendrimers were conical, rather than spherical. By modifying the shape of these series of dendrimer to almost spherical shape, a new serial of global-like dendrimer **G2-GL (n=2-4)** was constructed. It led to even higher macroscopic NLO effects (as high as 246 pm/V).<sup>1c</sup>



Scheme S1. The structures of dendrimers Gn (n=1-5), global-like dendrimers Gn-TPA and the related parameters:  $d_{33}$  (pm/V); PCs (numbers of chromophore pieces); N (%, the loading density of the effective chromophore moieties).<sup>1</sup>

The concept of isolation chromophore was then introduced to NLO dendrimers, **Gn-NS** (n=2-4) possessed a regular structure of alternating layers of nitro-based and sulfonyl-based azo chromophores, in which the sulfonyl-based azo-chromophore moieties were utilized as co-isolation groups for the nitro-based moieties to achieve larger macroscopic second-order nonlinear optical (NLO) effects. These high-generation dendrimers (**G4-NS** and **G5-NS**) displayed very large NLO efficiencies (up to 253.0 pm/V), which refreshed the new record.<sup>2</sup>



Scheme S2. "Isolation chromophore" introduced into dendrimer system to enhance NLO property.<sup>2</sup>
Perfluoroaromatic rings were introduced into dendrimers to further improve their performance.
Gn-F (n=1-5) were constructed based on the tree-like model, <sup>3a</sup> and Gn-GL-F (n=2-4) were built based on the global-like model.<sup>3b</sup>



Scheme S3. "Ar-ArF self-assembly effect" introduced into dendrimer system to enhance NLO

property.<sup>3</sup>

Both of the perfluoroaromatic rings and isolation chromophore were introduced into dendrimers to yield **Gn-NS-F** (n=1-5), constructed based on the tree-like model, <sup>3a</sup> and **Gn-GL-NS-F** (n=2-4) based on the global-like model.<sup>4</sup>



**Scheme S4**. "Isolation chromophore" and "Ar-ArF self-assembly effect" introduced into dendrimer system to enhance NLO property. <sup>3a,4</sup>

The above dendrimers were designed focusing on the molecular topology and functionalization. It turned out to be effective ways to enhance the NLO performance. Their NLO effect was improved step by step, but trapped around 250 pm/V. The new types of "X-type" NLO compounds, **D-5N** and **D-9N**, was recently reported.<sup>5</sup> In these dendrimers, chromophore moieties were arranged in order, and contributed a great deal to the good NLO performance of **D-5N** and **D-9N**: the  $d_{33}$  value of **D-5N** (containing only five chromophore moieties) was 157 pm/V, while that of **D-9N** (containing nine chromophore moieties) achieved 195 pm/V, at the same level of **G5** 



Scheme S5. The structures of "X" type dendrimers and the related parameters:  $d_{33}$  (pm/V); PCs (numbers of containing chromophore moiety pieces); N (%, the loading density of the effective chromophore moieties).<sup>5</sup>



## 2 NLO coefficient summarized to four quadrants

Fig. S1. Four quadrants:  $d_{33}$  value related to amount of chromophore moieties (chemical structure see Scheme S1-S4).

Quadrants I: large  $d_{33}$  value, high generation, and large amount of chromophore moieties Quadrants II: large  $d_{33}$  value, low generation, and small amount of chromophore moieties Quadrants III: small  $d_{33}$  value, and small amount of chromophore moieties Quadrants IV: small  $d_{33}$  value, low generation, and large amount of chromophore moieties

## **3 NLO Measurement**

#### 3.1 Second-order Nonlinear optical coefficients

The polarization  $p^{2\omega}$  in a nonlinear medium by an optical electric field  $E^{\omega}$  was stated as:<sup>6</sup>

$$p_i^{2\omega} = \chi_{ijk}^{2\omega} E_j^{\omega} E_k^{\omega}$$
(1)

 $\chi_{iik}^{2\omega}$  is a (3×3×3) third tensor, considering a particular physical situation, the two

symmetric suffixes *j* and *k* are replaced by a single suffix m, the relation is:

$$\frac{m=1}{jk=} \frac{2}{xx} \frac{3}{yy} \frac{4}{zz} \frac{5}{yz} \frac{6}{zx} \frac{6}{xy} \frac{6}{zx} \frac{1}{zx} \frac{6}{zx} \frac{1}{zx} \frac{1}{zx$$

It also can be described as:

$$\chi_{ijk}^{2\omega} \left(-2\omega_1; \omega_1\omega_1\right) = d_{ijk} \left(-2\omega_1; \omega_1\omega_1\right) \tag{3}$$

So the polarization *p* can be described as:

$$\begin{bmatrix} p_1 \\ p_2 \\ p_3 \end{bmatrix} = \epsilon_0 \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} E_1^2 \\ E_2^2 \\ E_3^2 \\ 2E_1 & E_3 \\ 2E_1 & E_2 \\ 2E_2 & E_3 \end{bmatrix}$$
(4)

For the sample lattice such as transparent crystals, if the absorption of fundamental beam or the second harmonic beam is negligible, the 18 independent coefficients can be condensed to 10:  $^7 d_{12} = d_{26}$ ,  $d_{13} = d_{35}$ ,  $d_{14} = d_{25} = d_{36}$ ,  $d_{15} = d_{31}$ ,  $d_{16} = d_{21}$ ,  $d_{23} = d_{34}$ ,  $d_{24} = d_{32}$ .

Therefore, in the most general cases, there are 10 independent coefficients as follows:

$$\begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{16} & d_{22} & d_{23} & d_{24} & d_{14} & d_{12} \\ d_{15} & d_{24} & d_{33} & d_{23} & d_{13} & d_{14} \end{bmatrix}$$
(5)

According to the Kleiman symmetry above, the  $SiO_2$ -quartz structure with  $D_3$  symmetry a typical example of the polar structure, has only one independent coefficient. In this paper,

Y-cut quartz serves as the reference, which dominates the  $d_{33}$  value of the samples by equation:<sup>8</sup>

$$\frac{d_{33,s}}{d_{11,q}} = \sqrt{\frac{I_s}{I_q}} \frac{l_{c,q}}{l_s} F$$
(6)

where  $d_{11,q}$  is the  $d_{11}$  of the quartz crystal (0.45 pm/V),  $I_s$  and  $I_q$  are the respective SHG intensities of the sample (polymer film) and the quartz crystal,  $l_{c,q}$  is the coherent length of the quartz crystal (20.6  $\mu$ m),  $l_s$  is the thickness of the sample, and *F* is the correction factor of the apparatus (1.2 when lc >> ls).

Within the two-level model of molecular nonlinearities, the resonantly enhanced hyperpolarizability can be expressed as:<sup>9</sup>

$$\beta(\omega) = \mathbf{R}(\omega) \times \beta_0 \tag{7}$$

Where  $\beta_0$  is the nonresonant value and the resonance enhancement factor is:

$$R(\omega) = \frac{\omega_0^{4}}{(\omega_0^{2} - \omega^{2}) \times (\omega_0^{2} - 4\omega^{2})}, \ \omega_0 = \frac{2\pi c}{\lambda_{\text{max}}}$$
(8)

Where  $\lambda_{max}$  is the wavelength at which the maximum of the principal absorption band occurs, and  $\omega$  corresponds to the wavelength of the laser.

 $d_{33(\infty)}$  was calculated using this approximate model:

$$d_{\infty} = d_{33} \times \left[ 1 - \left(\frac{\lambda_{\max}}{\lambda}\right)^2 \right] \times \left[ 1 - 4 \left(\frac{\lambda_{\max}}{\lambda}\right)^2 \right]$$
(9)

Where  $\lambda_{max}$  was the wavelength of maximum absorption,  $\lambda$  was the wavelength of the fundamental laser.

#### 3.2 Preparation of thin films

The samples were dissolved in THF (concentration  $\sim 3$  wt %), and the solutions were filtered through syringe filters. The thin films were spin-coated onto indium-tin-oxide (ITO)-coated glass substrates to form 200-250 nm thick films, the substrates were subjected to ultrasonication in different solvent systems including 2% soap in water, acetone, deionized water, DMF, THF. Each step was carried out for 20 min. Residual solvent of the thin films was removed by heating the films in a vacuum oven at  $45^{\circ}$ C.

#### **3.3 Measurement condition**

The second-order optical nonlinearity of the materials was determined by in-situ second harmonic generation (SHG) experiment by using a closed temperature-controlled oven with optical windows and three needle electrodes. The films were kept at 45° to the incident beam and poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature, different for each polymer; voltage, 7.0 kV at the needle point; gap distance, 0.8 cm. The SHG measurements were carried out with a Nd:YAG laser operating at a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm.

The NLO efficiencies were also investigated using 1950 nm laser radiation. The doubled frequency signals (975 nm) were detected by an Andor's DU420A-BR-DD CCD after the mixed signals passed through the monochromator.

#### 3.4 Error anylasis

The  $d_{33}$  values of these dendrimers were tested for several times under the same environment: room temperature  $25 \pm 1$  °C, humidity  $45 \pm 1$ %. They were also tested under the different environment: four environment conditions with small difference in room temperature ( $25 \pm 5$  °C) and humidity ( $45 \pm 5$ %). The  $d_{33}$  values were calculated by averaging the results measured in the two situations above.

Based on the measured results, we calculated the average deviation and the standard deviation (S). The average deviation (D) is calculated by using the following equation, where N is the number of tests,  $X_i$  is each value, X is the mean (average) value:

$$\mathbf{D} = \frac{\sum_{i=1}^{N} |\mathbf{X}i - \mathbf{X}|}{N}$$

The standard deviation (S) is calculated using the following equation, where N is the number of tests,  $X_i$  is each value, X is the mean (average) value:

$$S = \sqrt{\frac{\sum_{i=1}^{N} (Xi - X)^2}{N - 1}}$$

Under the 1064 nm fundamental beam, the average deviations are 25, 17 and 16 pm/V for D-13N, D-17N and D-21N, with the relatively average deviations of 8.4 %, 7.1 %, 6.4 % respectively. The standard deviations (S) values are 28, 20 and 22 pm/V for D-13N, D-17N and D-21N, with the relatively standard deviations of 9.5 %, 8.3 %, 8.4 % respectively. From the results, the relatively average deviations and relative standard deviations are all below 10 %.

Under the 1950 nm fundamental beam, the average deviations are 6, 6 and 7 pm/V for D-13N, D-17N and D-21N, with the relatively average deviations of 8.2 %, 9.9 % and 9.7 % respectively. The standard deviations (S) values are 8, 7 and 10 pm/V for D-13N, D-17N and D-21N, with the relatively standard deviations of 11.0 %, 12.2 %, 14.6 % respectively.

From the results under the 1064 nm fundamental beam, the relatively standard deviations are all below 10 %, while the values under 1950 nm fundamental beam are a little relatively high. The reason could be from the difference of the instruments.

To improve the comparison of the results, the samples from our other published papers were also tested. The results are listed below:

Sample	<i>d</i> <sub>33</sub> @1064	<i>d</i> <sub>33</sub> @1950	<i>d</i> <sub>33</sub> @1064	<i>d</i> <sub>33</sub> @1950
	(Published	(Published (test this		(test this
	before)	before)	time)	time)
D-13N	-	_	299	73
D-17N	-	_	238	63
D-21N	-	_	261	69
<b>D-5</b> N <sup>5</sup>	195	39	187	34
G3 <sup>1a</sup>	123	- 130		27
G2-TPA <sup>1b</sup>	219	_	205	39

From the results, we can see that the results of these three samples (**D-13N**, **D-17N** and **D-21N**) are reliable, especially in comparison with some typical samples from the previous work.

#### **4** Calculation

#### 4.1 Methods

The chromophore moiety (nitro-azo-benzene moiety) as the constructing unit for dendrimers, was firstly optimized by using DFT method with B3LYP functional<sup>10</sup> and 6-311G (d, p) basis set in vacuum. The quantum chemical calculations were performed in Gaussian 09 program package.<sup>11</sup> Then the moieties were used to construct the dendrimers. The configurations of dendrimer was calculated by using the molecular mechanics (MM) simulations in the Discover module from

Materials studio (MS) software package<sup>12</sup>. Herein, the polymer consistent force field (PCFF), was used to optimize structures, and the minimization method was Smart Minimizer. In addition, we failed to further optimize the structure of these dendrimers using quantum chemical calculations, even the semi-empirical calculation methods were unable to give a result.

#### 4.2 Results and discussion

Figure **S2-S4** showed the conformation of each dendrimer. It was obvious that the dendrimer was constructed from two dendrons (*x*-axis and *anti-x*-axis dendron), the two dendrons were of orthorhombic structure, the images were extracted from three viewpoints: Front-view, Side-view and Top-view. The viewpoint was based on the *x*-axis dendron. As easily seen, all the molecules had multi-azimuth 3D structures. Their conformation were almost spherical, and the orientation of the chromophore moieties on the molecular scale could be observed in the figure clearly. The original orientation of the chromophore moieties was very important for the final NLO effect. For **D-17N**, the dipolemoments in *x*-axis dendron counteracted with each other to a certain extent, but for **D-13N** and **D-21N**, the covalent bonds constrained the *x*-axis and *anti-x*-axis dendrons, and partially due to the steric hindrance, the dipolemoments did not counteract with each other too much. This might be the reason that **D-13N** and **D-21N** had much larger NLO effect.



Fig. S2 The optimized structure of D-13N viewed from different angles.



Fig. S3 The optimized structure of D-17N viewed from different angles.



Fig. S4 The optimized structure of D-21N viewed from different angles.

# **5** Experimental

## **5.1 Materials**

Tetrahydrofuran (THF) was dried over Na-K alloy and distilled under an atmosphere of dry nitrogen. *N*,*N*-Dimethylform amide (DMF) was dried over  $CaH_2$  and distilled under an atmosphere of dry nitrogen. Compound **R1**, **R2**, **R3**, **R4** were prepared according to our previous work<sup>13</sup>. All other reagents were used as received.

#### **5.2 Instrumentation**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Varian Mercury300, or Bruker BioSpin GmbH spectrometer using tetramethylsilane (TMS;  $\delta = 0$  ppm) as internal standard. UV-visible spectra were obtained using a Shimadzu UV-2550 spectrometer. The Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer-2 spectrometer in the region of 3000-400 cm<sup>-1</sup> on KBr pellets. Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer. MALDI-TOF mass spectrometer (MALDI-TOF MS; ABI, American) equipped with a 337 nm nitrogen laser and a 1.2 m linear flight path in positive ion mode. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 C/min in nitrogen at a flow rate of 50 cm<sup>3</sup>/min for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a METTLER differential scanning calorimeter DSC822e under nitrogen at a scanning rate of 10 °C/min. The thickness of the films was measured with an Ambios Technology **XP**-2 profilometer.

#### 5.3 Synthesis of *anti-x*-axis dendrons:



Scheme S6. Synthetic route to *anti-x*-axis dendron D-3N-2Azi<sup>13c</sup>



Scheme S7. Synthetic route to D-7N-Cl of *anti-x*-axis dendron

**Compound C1**: Compound **R1** (1.27 g, 0.05 mol) was dissolved in fluoboric acid (5 mL), the aqueous NaNO<sub>2</sub> solution (3 mL, 0.43 g) was then added in an ice water bath. After 12 hours, 20 mL of DMF was added into the mixture, and *N*-(2-chloroethyl)-*N*-ethylaniline (0.92 g, 0.5 mol) was also added dropwise. After the mixture was stirred at 0  $^{\circ}$  overnight, 100 mL of dichloromethane was

added into the reaction mixture, then DMF was washed out by water. The solvent was removed by evaporation under reduced pressure to afford the crude product, which was further purified by column chromatography on silica gel using dichloromethane as the eluent. Compound **C1** was yielded as red solid (1.89 g, 85.9 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.29-1.24 (m, 3H, -CH<sub>3</sub>), 1.65-1.48 (m, 6H, -CH<sub>2</sub>-), 1.95 (m, 2H, -CH<sub>2</sub>-), 3.57 (m, 2H, -CH<sub>2</sub>-), 3.67 (m, 4H, -CH<sub>2</sub>-), 3.73 (m, 2H, -NCH<sub>2</sub>-), 4.23 (t, *J*=6.6 Hz, 2H, -OCH<sub>2</sub>-), 6.77 (d, *J*=9.0 Hz, 2H, -ArH), 7.67 (m, 1H, -ArH), 7.92-7.86 (m, 4H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 155.19, 150.30, 148.14, 146.16, 144.52, 126.18, 117.24, 116.25, 111.25, 109.01, 69.82, 62.60, 52.11, 45.79, 40.12, 32.50, 28.86, 25.70, 25.37, 12.43. UV-vis (THF, 0.02 mg/mL):  $\lambda_{max}$  (nm): 470.

**Compound C2**: Compound **C1** (129.7 mg, 0.28 mmol) and Compound **R2** (133.1 mg, 0.57 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (221.9 mg, 1.1 mmol) 4-dimethylaminopyridine (DMAP) (14.1 mg, 0.1 mmol) were reacted in appropriate anhydrous CH<sub>2</sub>Cl<sub>2</sub> solution at 30 °C overnight under an atmosphere of dry nitrogen. The resultant mixture was washed by citric acid solution and water respectively for several times, the organic layer was combined, and dried over magnesium sulfate. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether (10/1) as the eluent. Compound **C2** was yielded as red solid (159.7 mg, 83.7 %).<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.27-1.22 (m, 3H, -CH<sub>3</sub>), 1.60-1.53 (m, 4H, -CH<sub>2</sub>-), 1.81 (m, 2H, -CH<sub>2</sub>-), 1.97 (m, 2H, -CH<sub>2</sub>-), 2.54 (d, 2H, -C=CH), 3.53 (m, 2H, -CH<sub>2</sub>-), 3.74-3.66 (m, 4H, -NCH<sub>2</sub>-), 4.24 (t, *J*=6.6 Hz, 2H, -OCH<sub>2</sub>-), 4.32 (t, *J*=6.6 Hz, 2H, -OCH<sub>2</sub>-), 4.70 (d, 4H, -CH<sub>2</sub>-), 6.79-6.74 (m, 3H, -ArH), 7.28 (s, 2H, -ArH), 7.67 (m, 1H, -ArH), 7.91-7.86 (m, 4H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 165.78, 158.38, 155.17, 150.30, 148.14, 146.82, 144.51, 132.36, 126.16, 117.21, 116.27, 108.98, 108.81, 106.98, 77.95, 76.02, 69.74, 65.07, 56.01, 52.09, 45.78, 40.19, 28.84, 28.51, 25.69, 12.43. UV-vis (THF, 0.02 mg/mL):  $\lambda_{max}$  (nm): 472.

**D-3N-Cl**: Compound **C2** (99.0 mg, 0.15 mmol), Compound **R3** (106.8 mg, 0.31 mmol), CuSO<sub>4</sub>  $5H_2O$  (10 mol %), NaHCO<sub>3</sub> (20 mol %), and ascorbic acid (20 mol %) were dissolved in DMF (10 mL)/H<sub>2</sub>O (0.8 mL) under nitrogen in a Schlenk flask. The mixture was stirred at 30 °C for 3 h, then extracted with chloroform, and washed with 1N HCl, 1N NH<sub>4</sub>OH and water subsequently. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using ethyl chloroform/ ethyl acetate (3/1) as

eluent to afford deep red solid (171.0 mg, 85.2%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.09 (m, 6H, -CH<sub>3</sub>), 1.24 (m, 3H, -CH<sub>3</sub>), 1.80 (m, 2H, -CH<sub>2</sub>-), 1.96 (m, 2H, -CH<sub>2</sub>-), 3.22 (m, 4H, -CH<sub>2</sub>-), 3.54 (m, 2H, -NCH<sub>2</sub>-), 3.71-3.67 (m, 4H, -NCH<sub>2</sub>-), 3.94 (m, 4H, -NCH<sub>2</sub>-), 4.22 (br, 2H, -OCH<sub>2</sub>-), 4.30 (br, 2H, -OCH<sub>2</sub>-), 4.60 (br, 4H, -NCH<sub>2</sub>-), 5.17 (s, 4H, -CH<sub>2</sub>-), 6.76-6.67 (m, 4H, -ArH), 7.55 (m, 2H, -ArH), 7.65 (m, 2H, -ArH), 7.93-7.80 (m, 12H, -CH<sub>2</sub>-), 8.30 (m, 4H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 158.99, 156.33, 154.92, 150.18, 147.49, 144.04, 133.53, 132.35, 132.35, 126.23, 124.57, 123.83, 122.63, 116.43, 111.41, 111.29, 108.65, 106.70, 65.26, 61.73, 50.35, 47.63, 45.83, 40.20, 28.99, 25.55, 12.48, 12.01. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 1715 (-C=O-); 1515, 1338 (-NO<sub>2</sub>). UV-vis (THF, 0.02 mg/mL):  $\lambda_{max}$  (nm): 466.

**D-3N-Azi: D-3N-CI** (175.0 mg, 0.13 mmol), NaN<sub>3</sub> (25.5 mg, 0.39 mmol) and DMF (7 mL) were added into a flask, the resultant mixture was allowed to stir at 80 °C overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, dried under vacuum, and purified by column chromatography using ethyl chloroform/ ethyl acetate (3/1) as eluent to yield deep red solid (170.3 mg, 96.8%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.09 (m, 6H, -CH<sub>3</sub>), 1.23 (m, 3H, -CH<sub>3</sub>), 1.80 (m, 2H, -CH<sub>2</sub>-), 1.96 (m, 2H, -CH<sub>2</sub>-), 3.22 (m, 4H, -CH<sub>2</sub>-), 3.59-3.52 (m, 6H, -NCH<sub>2</sub>-), 3.94 (m, 4H, -NCH<sub>2</sub>-), 4.22 (br, 2H, -OCH<sub>2</sub>-), 4.31 (br, 2H, -OCH<sub>2</sub>-), 4.60 (br, 4H, -NCH<sub>2</sub>-), 5.17 (s, 4H, -CH<sub>2</sub>-), 6.77-6.67 (m, 4H, -ArH), 7.24 (m, 2H, -ArH), 7.55 (m, 2H, -ArH), 7.64 (m, 2H, -ArH), 7.92-7.80 (m, 12H, -CH<sub>2</sub>-), 8.31 (m, 4H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 165.87, 159.02, 156.35, 155.14, 150.51, 150.21, 148.03, 147.36, 146.88, 144.45, 143.97, 143.63, 132.39, 126.28, 126.15, 124.53, 123.95, 122.74, 122.63, 117.19, 116.26, 111.35, 109.00, 108.64, 106.59, 69.72, 65.10, 61.92, 50.34, 49.41, 48.85, 47.62, 45.77, 28.76, 28.52, 25.65, 25.57, 12.18, 12.00. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 2102 (-N<sub>3</sub>); 1516, 1339 (-NO<sub>2</sub>). UV-vis (THF, 0.02 mg/mL):  $\lambda_{max}$  (nm): 467..

**D-7N-Cl: D-3N-Azi** (83.5 mg, 0.06 mmol), Compound **R4** (20.5 mg, 0.03 mmol), CuSO<sub>4</sub> 5H<sub>2</sub>O (10 mol %), NaHCO<sub>3</sub> (20 mol %), and ascorbic acid (20 mol %) were dissolved in DMF (4 mL)/H<sub>2</sub>O (0.3 mL) under nitrogen in a Schlenk flask. The mixture was stirred at 30 °C for 3 h, then extracted with chloroform, and washed with 1N HCl, 1N NH<sub>4</sub>OH and water subsequently. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using THF/chloroform (1/4) as eluent to afford deep red solid (70.5 mg, 70.5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.08 (m, 12H, -CH<sub>3</sub>), 1.25

(br, 6H, -CH<sub>3</sub>), 1.93-1.78 (br, 16H, -CH<sub>2</sub>-), 3.18 (br, 12H, -CH<sub>2</sub>-), 3.68 (br, 4H, -CH<sub>2</sub>-), 3.74 (br, 2H, -CH<sub>2</sub>-), 3.82 (br, 4H, -CH<sub>2</sub>-), 3.92 (br, 12H, -CH<sub>2</sub>-), 4.19 (br, 6H, -CH<sub>2</sub>-), 4.27 (br, 6H, -CH<sub>2</sub>-), 4.59 (br, 12H, -CH<sub>2</sub>-), 5.14 (br, 12H, -CH<sub>2</sub>-), 6.68-6.65 (m, 12H, -ArH), 6.74 (br, 6H, -ArH), 7.20 (m, 6H, -ArH), 7.61-7.58 (m, 8H, -ArH), 7.89-7.80 (m, 26H, -CH<sub>2</sub>-), 8.28 (m, 8H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 165.90, 159.03, 156.38, 155.08, 150.21, 148.09, 146.42, 144.05, 143.63, 132.44, 126.12, 124.52, 123.88, 122.62, 111.39, 109.13, 108.68, 69.35, 65.01, 61.93, 50.31, 47.61, 47.61, 45.80, 45.75, 28.74, 28.50, 25.64, 12.01.

**D-7N-Azi**: **D-7N-CI** (60.6 mg, 0.018 mmol), NaN<sub>3</sub> (6.9 mg, 0.10 mmol) and DMF (2.5 mL) were added into a flask, the resultant mixture was allowed to stir at 80 °C overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, dried under vacuum, and purified by column chromatography using chloroform/THF (4/1) as eluent to yield deep red solid (59.8 mg, 98.3%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.08 (m, 12H, -CH<sub>3</sub>), 1.78 (br, 6H, -CH<sub>2</sub>-), 1.93 (br, 6H, -CH<sub>2</sub>-), 3.18 (m, 12H, -CH<sub>2</sub>-), 3.56 (m, 4H, -CH<sub>2</sub>-), 3.92 (m, 12H, -CH<sub>2</sub>-), 4.19 (m, 6H, -CH<sub>2</sub>-), 4.28 (m, 6H, -CH<sub>2</sub>-), 4.59 (m, 12H, -NCH<sub>2</sub>-), 5.14 (m, 12H, -CH<sub>2</sub>-), 6.68-6.65 (m, 12H, -ArH), 6.75 (m, 6H, -ArH), 7.20 (br, 6H, -ArH), 7.62-7.58 (m, 9H, -ArH), 7.89-7.80 (m, 30H, -ArH), 8.28 (d, *J*=8.7 Hz, 8H, -ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 165.89, 159.00, 156.34, 155.44, 150.21, 149.97, 148.14, 147.37, 146.61, 144.59, 143.96, 143.59, 143.50, 132.33, 126.14, 126.04, 124.54, 124.05, 123.98, 122.63, 117.16, 116.19, 111.34, 108.93, 108.61, 106.52, 69.68, 65.11, 61.88, 50.32, 48.68, 47.60, 45.75, 28.73, 28.50, 25.63, 12.00. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 2099 (-N<sub>3</sub>); 1713 (-C=O-); 1515, 1338 (-NO<sub>2</sub>). UV -vis (THF, 0.02 mg/mL):  $\lambda_{max}$  (nm): 464.

#### 5.4 Synthesis of Janus dendrimers:



Scheme S8. Synthetic route to D-13N

**D-13N**: **D-7N-Azi** (51.0 mg, 0.015 mmol),  $G1 \equiv (63.8 \text{ mg}, 0.037 \text{ mmol})$ ,  $CuSO_4$  5H<sub>2</sub>O (10 mol %), NaHCO<sub>3</sub> (20 mol %), and ascorbic acid (20 mol %) were dissolved in DMF (5 mL)/H<sub>2</sub>O (0.4 mL) under nitrogen in a Schlenk flask. The mixture was stirred at 30 °C for 4 h, then extracted with chloroform, and washed with 1N HCl, 1N NH<sub>4</sub>OH and water subsequently. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using THF/chloroform (1/2) as eluent to afford deep red solid (90.1 mg, 88.3%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K), δ (TMS, ppm): 1.04 (m, 18H, -CH<sub>3</sub>), 1.25 (br, 16H, -CH<sub>3</sub>), 1.75 (br, 8H, -CH<sub>2</sub>-), 1.91 (br, 12H, -CH<sub>2</sub>-), 2.19 (br, 16H, -CH<sub>2</sub>-), 2.90 (br, 30H, -CH<sub>2</sub>-), 3.90 (br, 6H, -CH<sub>2</sub>-), 3.18 (br, 16H, -CH<sub>2</sub>-), 3.70 (br, 16H, -CH<sub>2</sub>-), 3.90 (br, 28H, -CH<sub>2</sub>-), 4.09 (br, 18H, -CH<sub>2</sub>-), 4.25 (br, 6H, -CH<sub>2</sub>-), 4.36 (br, 16H, -CH<sub>2</sub>-), 4.58-4.54 (m, 26H, -CH<sub>2</sub>-), 5.09 (s, 4H, -CH<sub>2</sub>-), 5.13 (s, 8H, -CH<sub>2</sub>-), 6.49 (m, 4H, -ArH), 6.65 (m, 12H, -ArH), 6.71 (m, 4H, -ArH), 6.91 (m, 8H, -ArH), 7.14 (br, 2H, -ArH), 7.19 (br, 4H, -ArH), 7.30 (m, 4H, -ArH), 7.42-7.37 (m, 18H, -ArH), 7.86-7.50(m, 84H, -ArH), 7.97 (m, 16H, -ArH), 8.23 (d, J=8.4 Hz, 4H, -ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K), δ (ppm): 166.35, 165.86, 159.01, 126.33, 155.19, 155.00, 150.74, 150.22, 148.27, 148.10, 147.35, 147.03, 146.73, 146.62, 144.82, 143.95, 143.57, 135.64, 133.20, 126.50, 128.40, 126.11, 125.90, 124.52, 123.99, 122.60, 122.38, 117.30, 117.07, 116.34, 116.15, 111.80, 111.66, 111.54, 111.35, 109.17, 68.49, 65.11, 61.88, 61.62, 50.31, 49.80, 47.60, 47.15, 45.75, 29.60, 28.73, 28.49, 25.64, 21.72, 12.00. MALDI-TOF MS: calcd for (C<sub>351</sub>H<sub>350</sub>N<sub>88</sub>O<sub>63</sub>): m/z

[M+Na]<sup>+</sup>: 6826; found: *m*/*z* 6820. (EA) (%, found/Calcd): C, 61.77/61.91; H, 5.33/5.18; N, 17.91/18.10. R (KBr), v (cm<sup>-1</sup>): 1717 (-C=O-); 1516, 1339 (-NO<sub>2</sub>). UV-vis (THF, 0.02 mg/mL):  $\lambda_{max}$ (nm): 463.



Scheme S9. Synthetic route to D-17N

D-5N-Cl: Compound D-3N-2Azi (30.3 mg, 0.02 mmol), Compound R5 (20.6 mg, 0.05 mmol), CuSO<sub>4</sub> 5H<sub>2</sub>O (10 mol %), NaHCO<sub>3</sub> (20 mol %), and ascorbic acid (20 mol %) were dissolved in DMF (3 mL)/H<sub>2</sub>O (0.3 mL) under nitrogen in a Schlenk flask. The mixture was stirred at 30 °C for 3 h, then extracted with chloroform, and washed with 1N HCl, 1N NH<sub>4</sub>OH and water subsequently. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using THF/chloroform (1/3) as eluent to afford deep red solid (44.2 mg, 88.4%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.09 (t, 6H, J=6.9 Hz, -CH<sub>3</sub>), 1.25 (br, 2H, -CH<sub>2</sub>-), 1.80 (m, 2H, -CH<sub>2</sub>-), 1.94 (br, 28H, -CH<sub>2</sub>-), 2.22 (m, 4H, -CH<sub>2</sub>-), 2.94 (m, 4H, -CH<sub>2</sub>-), 3.20 (m, 4H, -CH<sub>2</sub>-), 3.68 (m, 10H, -CH<sub>2</sub>-), 3.83 (m, 12H, -CH<sub>2</sub>-), 3.92 20

(m, 4H, -CH<sub>2</sub>-), 4.14 (m, 6H, -CH<sub>2</sub>-), 4.28 (m, 2H, -CH<sub>2</sub>-), 4.38 (m, 4H, -CH<sub>2</sub>-), 4.60 (m, 4H, -CH<sub>2</sub>-), 5.13 (s, 4H, -CH<sub>2</sub>-), 6.58 (d, *J*=9.0 Hz, 2H, -ArH), 6.66 (d, *J*=9.3 Hz, 3H, -ArH), 6.73 (d, *J*=9.0 Hz, -ArH), 7.16 (br, 2H, -ArH), 7.62-7.53 (m, 4H, -ArH), 7.89-7.75 (m, 20H, -ArH), 8.26 (d, *J*=9.0 Hz, 4H, -ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 165.90, 158.99, 156.31, 155.58, 155.11, 150.21, 149.48, 145.05, 143.97, 143.59, 132.10, 126.18, 126.10, 125.4, 123.95, 122.62, 122.12, 117.34, 116.34, 111.59, 111.38, 109.15, 108.47, 106.64, 68.48, 64.85, 61.90, 53.31, 51.37, 50.32, 47.62, 45.77, 40.12, 29.61, 28.34, 25.89, 21.71, 12.02. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 1515, 1339 (-NO<sub>2</sub>). UV-vis (THF, 0.02 mg/mL):  $\lambda_{max}$  (nm): 457.

**D-5N-Azi: D-5N-CI** (35.3 mg, 0.015 mmol), NaN<sub>3</sub> (12.0 mg, 0.18 mmol) and DMF (2 mL) were added into a flask, the resultant mixture was allowed to stir at 80 °C overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, dried under vacuum, and purified by column chromatography using ethyl chloroform/THF (3/1) as eluent to yield deep red solid (30.0 mg, 83.9%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.09 (t, 6H, *J*=6.9 Hz, -CH<sub>3</sub>), 1.25 (br, 2H, -CH<sub>2</sub>-), 1.79 (m, 2H, -CH<sub>2</sub>-), 1.95 (br, 28H, -CH<sub>2</sub>-), 2.22 (m, 4H, -CH<sub>2</sub>-), 2.94 (m, 4H, -CH<sub>2</sub>-), 3.20 (m, 4H, -CH<sub>2</sub>-), 3.57 (m, 10H, -CH<sub>2</sub>-), 3.68 (m, 12H, -CH<sub>2</sub>-), 3.93 (m, 4H, -CH<sub>2</sub>-), 4.14 (m, 6H, -CH<sub>2</sub>-), 4.28 (m, 2H, -CH<sub>2</sub>-), 4.38 (m, 4H, -CH<sub>2</sub>-), 4.60 (m, 4H, -CH<sub>2</sub>-), 5.13 (s, 4H, -CH<sub>2</sub>-), 6.58 (d, *J*=9.0 Hz, 2H, -ArH), 6.66 (d, *J*=9.3 Hz, 3H, -ArH), 6.78 (d, *J*=9.0 Hz, -ArH), 7.17 (br, 2H, -ArH), 7.29(br, 2H, -ArH), 7.59-7.53 (m, 4H, -ArH), 7.89-7.12 (m, 20H, -ArH), 8.26 (d, *J*=9.0 Hz, 4H, -ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 165.77, 159.00, 155.07, 150.37, 149.79, 147.01, 146.61, 144.96, 144.22, 143.93, 126.47, 126.10, 124.57, 122.55, 117.34, 116.38, 111.81, 111.65, 111.56, 109.50, 108.47, 68.49, 61.73, 56.89, 50.64, 50.38, 48.68, 47.60, 47.52, 47.37, 46.20, 28.32, 21.29, 12.01. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 2100 (-N<sub>3</sub>); 1516, 1339 (-NO<sub>2</sub>). UV-vis (THF, 0.02 mg/mL):  $\lambda_{max}$  (nm): 461.

**D-17N**: **D-5N-Azi** (23.1 mg, 0.01 mmol),  $G1 \equiv (81.3 \text{ mg}, 0.05 \text{ mmol})$ ,  $CuSO_4 5H_2O (10 \text{ mol }\%)$ , NaHCO<sub>3</sub> (20 mol %), and ascorbic acid (20 mol %) were dissolved in DMF (4.5 mL)/H<sub>2</sub>O (0.3 mL) under nitrogen in a Schlenk flask. The mixture was stirred at 30 °C for 3 h, then extracted with chloroform, and washed with 1N HCl, 1N NH<sub>4</sub>OH and water subsequently. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using THF/chloroform (1/2) as eluent to afford deep red solid (81.2 mg, 89.0%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.04 (t, 6H, *J*=6.9 Hz, -CH<sub>3</sub>), 1.25 (br, 4H, -CH<sub>2</sub>-), 2.17 (br, 28H, -CH<sub>2</sub>-), 2.89 (br, 28H, -CH<sub>2</sub>-), 3.18 (br, 4H, -CH<sub>2</sub>-), 3.70 (br, 30H, -CH<sub>2</sub>-), 3.90 (br, 36H, -CH<sub>2</sub>-), 4.06 (br, 30H, -CH<sub>2</sub>-), 4.37 (br, 28H, -CH<sub>2</sub>-), 4.53 (br, 34H, -CH<sub>2</sub>-), 5.12 (s, 4H, -CH<sub>2</sub>-), 6.50-6.48 (m, 10H, -ArH), 6.63-6.60 (m, 5H, -ArH), 6.92-6.90 (m, 15H, -ArH), 7.15 (br, 2H, -ArH), 7.32(m, 8H, -ArH), 7.44-7.36 (m, 50H, -ArH), 7.68-7.50(m, 54H, -ArH), 7.78-7.71 (m, 14H, -ArH), 7.85-7.82 (m, 18H, -ArH), 7.98-7.95 (m, 30H, -ArH), 8.18-8.15 (d, *J*=9.0 Hz, 4H, -ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K), δ (ppm): 166.34, 159.02, 155.17, 155.01, 150.78, 148.23, 148.10, 147.04, 146.74, 146.09, 145.05, 144.99, 144.96, 144.83, 133.18, 129.49, 128.38, 126.07, 125.87, 122.57, 122.40, 117.30, 116.34, 111.83, 111.54, 111.35, 109.20, 68.55, 61.64, 51.06, 49.79, 47.16, 47.16, 28.53, 28.34, 21.70. MALDI-TOF MS: calcd for (C<sub>473</sub>H<sub>458</sub>N<sub>116</sub>O<sub>85</sub>): *m/z* [M+Na]<sup>+</sup>: 9145; found: *m/z* 9145. (EA) (%, found/Calcd): C, 62.03/62.24; H, 5.28/5.06; N, 17.82/17.80. IR (KBr), ν (cm<sup>-1</sup>):1717 (-C=O-); 1519, 1339 (-NO<sub>2</sub>). UV-vis (THF, 0.02 mg/mL): λ<sub>max</sub> (nm): 460.

**D-9N-Cl: D-7N-Azi** (82.7 mg, 0.024 mmol), Compound **R5** (22.8 mg, 0.051 mmol), CuSO<sub>4</sub> 5H<sub>2</sub>O (10 mol %), NaHCO<sub>3</sub> (20 mol %), and ascorbic acid (20 mol %) were dissolved in DMF (3 mL)/H<sub>2</sub>O (0.3 mL) under nitrogen in a Schlenk flask. The mixture was stirred at 30 °C for 4 h, then extracted with chloroform, and washed with 1N HCl, 1N NH<sub>4</sub>OH and water subsequently. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using THF/chloroform (1/3) as eluent to afford deep red solid (86.0 mg, 82.4 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K), δ (TMS, ppm): 1.08 (m, 12H, -CH<sub>3</sub>), 1.25 (m, 6H, -CH<sub>3</sub>), 1.78 (br, 6H, -CH<sub>2</sub>-), 1.93 (br, 6H, -CH<sub>2</sub>-), 2.21 (br, 4H, -CH<sub>2</sub>-), 2.94 (br, 6H, -CH<sub>2</sub>-), 3.19 (m, 12H, -CH<sub>2</sub>-), 3.68 (m, 12H, -CH<sub>2</sub>-), 3.80 (m, 6H, -CH<sub>2</sub>-), 3.92 (m, 12H, -CH<sub>2</sub>-), 4.18-4.13 (m, 10H, -CH<sub>2</sub>-), 4.28 (m, 6H, -CH<sub>2</sub>-), 4.38 (m, 4H, -CH<sub>2</sub>-), 4.60 (m, 12H, -CH<sub>2</sub>-), 5.14-5.09 (m, 12H, -CH<sub>2</sub>-), 6.68-6.65 (m, 12H, -ArH), 6.74-6.71 (m, 6H, -ArH), 7.19-7.15 (br, 6H, -ArH), 7.31 (br, 3H, -ArH), 7.60-7.54 (m, 10H, -ArH), 7.88-7.65 (m, 36H, -ArH), 8.27-8.24 (m, 8H, -ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K), δ (ppm): 165.88, 185.98, 156.29, 155.17, 155.10, 450.21, 149.98, 149.47, 148.26, 147.30, 146.55, 146.47, 144.98, 144.54, 143.90, 143.56, 143.40, 132.31, 126.15, 125.94, 124.53, 124.13, 124.03, 122.60, 117.21, 117.12, 116.30, 116.18, 111.56, 111.32, 109.08, 108.85, 108.85, 108.58, 106.49, 69.64, 68.46, 67.76, 65.12, 61.86, 53.26, 50.32, 47.60, 45.77, 40.14, 28.73, 28.49, 25.64, 21.82, 12.01. IR (KBr), v (cm<sup>-1</sup>): 1716 (-C=O-); 1516, 1338 (-NO<sub>2</sub>). UV-vis (THF, 0.02 mg/mL):  $\lambda_{max}$  (nm): 463.



Scheme S10. The synthetic route to D-21N

**D-9N-Azi**: **D-9N-Cl** (70.0 mg, 0.016 mmol), NaN<sub>3</sub> (15.8 mg, 0.24 mmol) and DMF (5 mL) were added into a flask, the resultant mixture was allowed to stir at 80 °C overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, dried under vacuum, and purified by column chromatography using chloroform/THF (3/1) as eluent to yield deep red solid (66.7 mg, 94.7%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.07 (m, 12H, -CH<sub>3</sub>), 1.77 (br, 6H, -CH<sub>2</sub>-), 1.91 (br, 6H, -CH<sub>2</sub>-), 2.21 (br, 4H, -CH<sub>2</sub>-), 2.93 (br, 6H, -CH<sub>2</sub>-), 3.18 (m, 12H, -CH<sub>2</sub>-), 3.55 (m, 12H, -CH<sub>2</sub>-), 3.67 (m, 6H, -CH<sub>2</sub>-), 3.92 (m, 12H, -CH<sub>2</sub>-), 4.18-4.12 (m, 10H,

-CH<sub>2</sub>-), 4.27 (m, 6H, -CH<sub>2</sub>-), 4.37 (m, 4H, -CH<sub>2</sub>-), 4.60 (m, 12H, -CH<sub>2</sub>-), 5.13-5.09 (m, 12H, -CH<sub>2</sub>-), 6.67-6.64 (m, 12H, -ArH), 6.77-6.74 (m, 6H, -ArH), 7.19-7.15 (br, 6H, -ArH), 7.30 (br, 3H, -ArH), 7.60-7.53 (m, 10H, -ArH), 7.88-7.65 (m, 36H, -ArH), 8.26-8.23 (m, 8H, -ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 165.88, 158.99, 156.27, 155.17, 155.06, 150.23, 150.00, 149.74, 148.16, 148.04, 147.23, 147.03, 146.50, 144.87, 144.49, 142.84, 142.51, 143.39, 132.29, 126.13, 152.94, 124.52, 124.10, 122.60, 122.38, 117.23, 117.08, 117.03, 116.16, 111.74, 111.55, 111.30, 109.04, 108.83, 108.56, 106.48, 69.63, 68.45, 65.13, 61.83, 50.57, 50.32, 48.62, 47.59m 47.74m 28.73m 28.49, 28.38, 25.64, 21.73, 11.99. IR (KBr), v (cm<sup>-1</sup>): 2100 (-N<sub>3</sub>); 1713 (-C=O-); 1515, 1338 (-NO<sub>2</sub>). UV-vis (THF, 0.02 mg/mL):  $\lambda_{max}$  (nm): 465.

**D-21N: D-9N-Azi** (43.3 mg, 0.01 mmol), **G1** $\equiv$  (102.2 mg, 0.06 mmol), CuSO<sub>4</sub> 5H<sub>2</sub>O (10 mol %), NaHCO<sub>3</sub> (20 mol %), and ascorbic acid (20 mol %) were dissolved in DMF (7 mL)/H<sub>2</sub>O (0.5 mL) under nitrogen in a Schlenk flask. The mixture was stirred at 30 °C for 10 h, then extracted with chloroform, and washed with 1N HCl, 1N NH<sub>4</sub>OH and water subsequently. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using THF as eluent to afford deep red solid (97.2 mg, 87.4%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K), δ (TMS, ppm): 1.05 (-CH<sub>3</sub>), 1.25 (-CH<sub>2</sub>-), 1.85 (-CH<sub>2</sub>-), 2.17 (-CH<sub>2</sub>-), 2.90 (-CH<sub>2</sub>-), 3.15 (-CH<sub>2</sub>-), 3.74 (-CH<sub>2</sub>-), 3.90 (-CH<sub>2</sub>-), 4.07 (-CH<sub>2</sub>-), 4.25 (-CH<sub>2</sub>-), 4.36 (-CH2-), 4.53 (-CH2-), 5.13 (-CH2-), 6.50 (-ArH), 6.64-6.62 (-ArH), 6.73 (-ArH), 6.92-6.89 (-ArH), 7.18 (-ArH), 7.31 (-ArH), 7.39 (-ArH), 7.52(-ArH), 7.61 (-ArH), 7.67 (-ArH), 7.82-7.72 (-ArH), 7.97-7.95 (-ArH), 8.19 (-ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 166.35, 165.78, 158.99, 156.26, 155.15, 154.98, 150.73, 150.23, 149.27, 148.14, 147.21, 147.01, 146.62, 145.98, 144.96, 144.74, 143.83, 143.50, 133.22, 132.22, 132.28, 129.49, 129.40, 126.10, 125.90, 124.51, 124.13, 122.59, 122.46, 117.23, 117.04, 116.31, 116.14, 111.76, 111.64, 111.45, 111.29, 109.05, 108.57, 106.53, 98.48, 77.36, 77.05, 76.73, 69.53, 68.41, 67.87, 67.13, 61.83, 61.63, 51.07, 51.04, 50.31, 49.75, 47.58, 47.14, 45.73, 33.23, 28.72, 28.49, 28.41, 28.33, 25.63, 25.63, 25.51, 23.30, 21.70, 11.99. MALDI-TOF MS: calcd for  $(C_{575}H_{566}N_{144}O_{103})$ : m/z [M+Na]<sup>+</sup>: 11134; found: m/z11139. (EA) (%, found/Calcd): C, 62.06/61.99; H, 5.32/5.12; N, 17.92/18.10. IR (KBr), v (cm<sup>-1</sup>): 1717 (-C=O-); 1516, 1339 (-NO<sub>2</sub>). UV-vis (THF, 0.02 mg/mL): λ<sub>max</sub> (nm): 462.

# 5.5 <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra



Fig.S6. <sup>1</sup>H NMR spectrum of compound D-13N in chloroform-*d*.



Fig.S7. <sup>13</sup>C NMR spectrum of compound D-13N in chloroform-*d*.



Fig.S8. <sup>1</sup>H NMR spectrum of compound D-17N in chloroform-d.



Fig.S9. <sup>13</sup>C NMR spectrum of compound **D-17N** in chloroform-*d*.





Fig.S11. <sup>13</sup>C NMR spectrum of compound D-21N in chloroform-*d*.





Fig.S13. <sup>13</sup>C NMR spectrum of compound D-5N-Azi in chloroform-*d*.



Fig.S15. <sup>13</sup>C NMR spectrum of compound D-5N-Cl in chloroform-*d*.





Fig.S17. <sup>13</sup>C NMR spectrum of compound D-7N-Azi in chloroform-*d*.



Fig.S19. <sup>13</sup>C NMR spectrum of compound D-7N-Cl in chloroform-d.



Fig.S21. <sup>13</sup>C NMR spectrum of compound D-3N-Azi in chloroform-*d*.



Fig.S23. <sup>13</sup>C NMR spectrum of compound D-9N-Azi in chloroform-*d*.



**Fig.S24**. <sup>1</sup>H NMR spectrum of compound **D-9N-Cl** in chloroform-*d*.



Fig.S25. <sup>13</sup>C NMR spectrum of compound D-9N-Cl in chloroform-*d*.



Fig.S27. <sup>13</sup>C NMR spectrum of compound D-3N-CL in chloroform-*d*.



Fig.S28. <sup>1</sup>H NMR spectrum of compound C2 in chloroform-*d*.



Fig.S29. <sup>13</sup>C NMR spectrum of compound C2in chloroform-*d*.



Fig.S31. <sup>13</sup>C NMR spectrum of compound C1 in chloroform-*d*.

## 5.6 MALDI-TOF Mass spectra









Fig.S33. The MALDI-TOF mass spectrum of D-17N.

Fig.S34. The MALDI-TOF mass spectrum of D-21N.

#### 5.7 GPC analysis

All the polydispersity  $(M_w/M_n)$  of these three dendrimers, measured by GPC, were close to 1, and the peaks were very sharp and narrow even compared to the polystyrene standard. The instrument parameters were listed as:

Inject volume : 20.000 µL **Concentration**: 1.000 g/L Calibration : LIZHEN-1-THF.CAL Calibration MH-K : 1.000000 ml/g univ. Calibration MH-K: 0.000000 ml/g Calibration MH-A: 0.000000 univ. Calibration MH-A: 0.000000 \_ \_ Internal Standard Calibration : 50.000 ml Data Interval : 0.290 s Eluent : **THF100 %** Flow: 1.000 ml/min Temperature : 23.000 C

Detector 1 : vwd1	A Delay :	0.000 ml
Baseline from :	7.934 to :	8.980 min
Integration from :	7.934 to :	8.980 min

## Table S1. The GPC results

	D-13N	D-17N	D-21N	PS
<i>M</i> <sub>n</sub> : g/mol	6.690E+3	7.361E+3	9.092E+3	1.102E+4
<i>M</i> <sub>w</sub> : g∕mol	6.924E+3	7.745E+3	9.562E+3	1.194E+4
<i>M</i> <sub>z</sub> : g/mol	7.129E+3	8.044E+3	1.015E+4	1.256E+4
<i>M</i> <sub>v</sub> : g/mol	0.000E+0	0.000E+0	0.000E+0	0.000E+0
<i>D</i> :	1.035E+0	1.052E+0	1.052E+0	1.084E+0
[n]: ml/g	0.000E+0	0.000E+0	0.000E+0	0.000E+0
V <sub>p</sub> : ml	8.377E+0	8.309E+0	8.231E+0	7.916E+0
<i>M</i> <sub>p</sub> : g/mol	7.064E+3	8.004E+3	9.220E+3	1.203E+4
A: ml*V	3.446E+1	6.146E+1	9.949E+1	3.423E+2
10% : g/mol	5.4593e3	5.9251e3	7.2178e3	8.7921e3
30% : g/mol	6.3731e3	7.1140e3	8.4029e3	1.0561e4
60% : g/mol	7.2241e3	8.1292e3	9.6648e3	1.2457e4
85% : g/mol	8.0952e3	9.1529e3	1.1237e4	1.4564e4
90% : g/mol	8.3794e3	9.4889e3	1.1955e4	1.5277e4



**Fig.S35** (a) **D-13N**, (b) **D-17N**, (c) **D-21N** and standard (d) polystyrene (commercial available,  $M_w$  =13880,  $M_w/M_n$ =1.02), tested here:  $M_w$  =11940,  $M_w/M_n$ =1.08.

## 5.8 Thermal analysis



Fig. S36. TGA thermograms of dendrimers measured in nitrogen at a heating rate of 10 °C/min.



Fig. S37. DSC thermograms of dendrimers measured in nitrogen at a heating rate of 10 °C/min

## 5.9 IR and UV-vis analysis





Fig. S39UV-vis spectra of dendrimers containing different chromophore moieties in THF.



Fig. S40 UV-vis absorption spectra of D-13N in different solvents.



Fig. S41UV-vis absorption spectra of D-17N in different solvents.



Fig. S42 UV-vis absorption spectra of D-21N in different solvents.



Fig. S43 UV-vis absorption spectra of C1 in different solvents.

**Table S2**. The maximum absorption wavelength ( $\lambda_{max}$ , nm) in different solvents (0.02 mg/mL)

	1,4-dioxane	CHCl <sub>3</sub>	THF	CH <sub>2</sub> Cl <sub>2</sub>	DMF	DMSO	Δ
D-13N	458	458	463	461	476	482	24
<b>D-17N</b>	455	458	460	459	473	482	27
<b>D-21N</b>	457	457	462	458	474	481	24
C1	464	474	470	476	488	498	34

 $\Delta = \lambda_{max}$ (in DMSO) - $\lambda_{max}$ (in 1,4-dioxane)

## 5.10 UV-vis spectra of thin film before and after poling



Fig. S44 UV-vis absorption spectra of thin film before and after poling

## **6** References

- (a) Z. Li, G. Yu, W. Wu, Y. Liu, C. Ye, J. Qin and Z. Li, *Macromolecules*, 2009, 42, 3864; (b) Z. Li, W. Wu, Q. Li, G. Yu, L. Xiao, Y. Liu, C. Ye, J. Qin and Z. Li, *Angew. Chem. Int. Ed.*, 2010, 49, 2763. (c) W. Wu, L. Huang, C. Song, G. Yu, C. Ye, Y. Liu, J. Qin, Q. Li and Z. Li, *Chem. Sci.*, 2012, 3, 1256-1261.
- 2 W. Wu, C. Li, G. Yu, Y. Liu, C. Ye, J. Qin and Z. Li, *Chem. Eur. J*, 2012, **18**, 11019.
- 3 (a) W. Wu, G. Yu, Y. Liu, C. Ye, J. Qin and Z. Li, *Chem. Eur. J*, 2013, **19**, 630; (b) W. Wu, C. Wang, R. Tang, Y. Fu, C. Ye, J. Qin and Z. Li, *J. Mater. Chem. C*, 2013, **1**, 717.
- 4 W. Wu, C. Ye, J. Qin and Z. Li, ACS App. Mater. Inter., 2013, 5, 7033.
- 5 R. Tang, S. Zhou, W. Xiang, Y. Xie, H. Chen, Q. Peng, G. Yu, B. Liu, H. Zeng, Q. Li and Z. Li, *J. Mater. Chem. C*, 2015, **3**, 4545.
- 6 P. A. Franken, J. F. Ward, *Rev. Mod. Phys.* 1963, **35**, 23.
- 7 D. A. Kleiman, *Phys. Rev.* 1962, **126**, 1977.
- 8 (a) D. N. Nikogosyan, Nonlinear Optical Crystals: A Complete Survey; Springer: New York, 2005. (b) P. Günter, Nonlinear Optical Effects and Materials; Springer: Berlin, 2000.
- 9 M. Kauranen, C. Boutton, T. Verbiest, M. N. Teerenstra, K. Clays, A. J. Schouten, R. J. M. Nolte, A. Persoons, *Science.*, 1995, 270, 966.

- 10 (a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648. (b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785.
- Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- (a) Yang, H.; Fang, F.; Zhao, C.; Li, D.; Li, J.; Sun, J.; Du, Q.; Zhu, H., *Med. Chem. Commun.* 2014, *5*, 219. (b)
   Tian, W.; Ma, Y.; *Chem. Soc. Rev.* 2013, *42*, 705.
- (a) Z. Li, Z. Li, C. Di, Z. Zhu, Q. Li, Q. Zeng, K. Zhang, Y. Liu, C. Ye, J. Qin, *Macromolecules*, 2006, 39, 6951; (b) Z. Li, Q. Zeng, Z. Li, S. Dong, Z. Zhu, Q. Li, C. Ye, C. Di, Y. Liu, J. Qin, *Macromolecules*, 2006, 39, 8544.
- 14 C. Reichardt, Chem. Soc. Rev. 1992, 21, 147.