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**Electronic Supplementary Information for:**

# Janus NLO dendrimers with different periphery functional groups: convenient synthesis and the enhanced NLO performance with the aid of the Ar-Ar$^F$ self-assembly

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## Error anylasis

To ensure the reliability of the test results, average values were obtained through test at least from three films for every sample and three times for each film. The $d_{33}$ values of these dendrimers were tested under the same environment: room temperature 25 ±1 $^{o}$C, humidity 40 ±1%.

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

$$\mathrm{A.D.} = \frac{\sum_{i=1}^{N}|X_i - X|}{N}$$

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 average value:

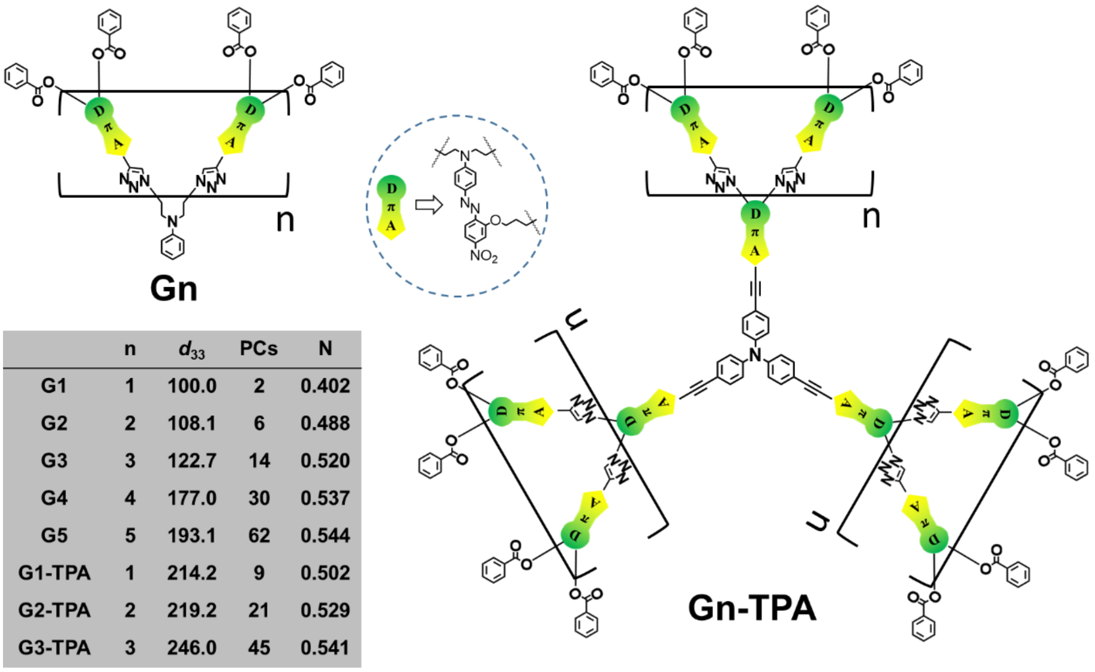
$$\mathrm{S} = \sqrt{\frac{\sum_{i=1}^{N}(X_i - X)^2}{N-1}}$$

Under the 1064 nm fundamental beam, the average deviations (A.D.) are 8.0, 6.9 and 4.2 pm/V for **S1-Ph**, **J1** and **S1-PFPh**, with the relatively average deviations of 7.1 %, 5.8 %, 4.1 % respectively. The standard deviations (S) values are 10.4, 9.2 and 6.3 pm/V for **S1-Ph**, **J1** and **S1-PFPh**, with the relatively standard deviations of 9.2 %, 7.8 %, 6.2 % respectively. From the results, the relatively average deviations and relative standard deviations are all below 10 %.

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

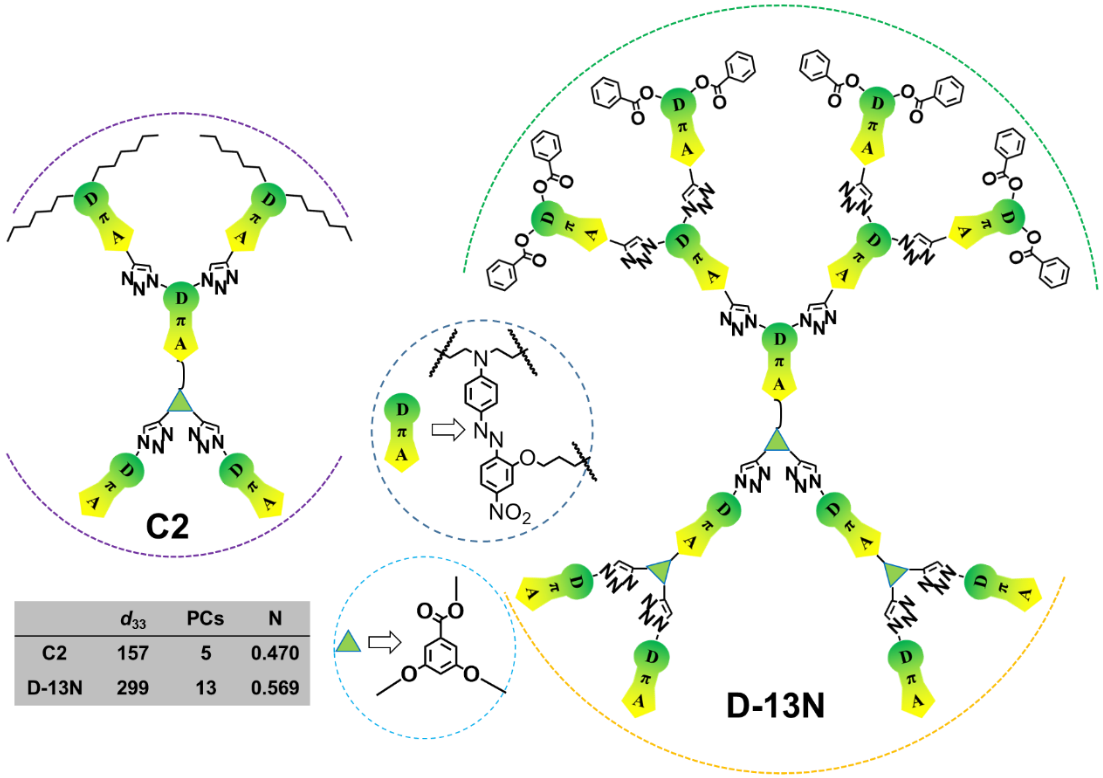
| Sample | **S1-Ph** | **J1** | **S1-PFPh** | **G1**[1] | **C3**[2] | **D-17N**[3] |
|---|---|---|---|---|---|---|
| $d_{33}$ (published before) | — | — | — | 100.0 | 195.2 | 238.0 |
| $d_{33}$ (test this time) | 112.8 | 118.0 | 101.3 | 110.3 | 193.5 | 220.5 |

From the results, we can see that the results of these three samples (**S1-Ph**, **J1** and **S1-PFPh**) are reliable, especially in comparison with some typical samples from the previous work.



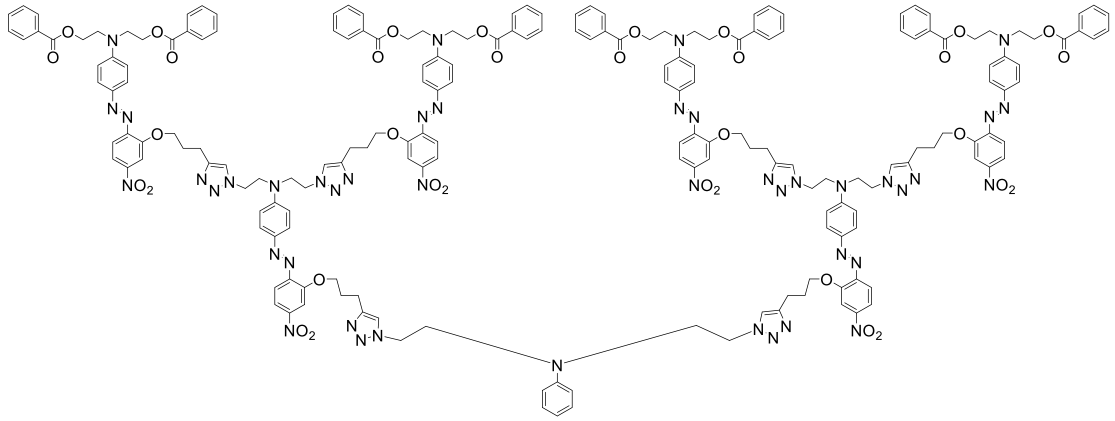
| | n | $d_{33}$ | PCs | N |
|---|---|---|---|---|
| G1 | 1 | 100.0 | 2 | 0.402 |
| G2 | 2 | 108.1 | 6 | 0.488 |
| G3 | 3 | 122.7 | 14 | 0.520 |
| G4 | 4 | 177.0 | 30 | 0.537 |
| G5 | 5 | 193.1 | 62 | 0.544 |
| G1-TPA | 1 | 214.2 | 9 | 0.502 |
| G2-TPA | 2 | 219.2 | 21 | 0.529 |
| G3-TPA | 3 | 246.0 | 45 | 0.541 |

**Scheme S1**. The structures of conical dendrimers Gn (n = 1-5)[1,4], global-like dendrimers Gn-TPA[5] and their related parameters: $d_{33}$ (pm/V); PCs (numbers of containing chromophore moiety pieces); N (%, the loading density of the effective chromophore moieties).

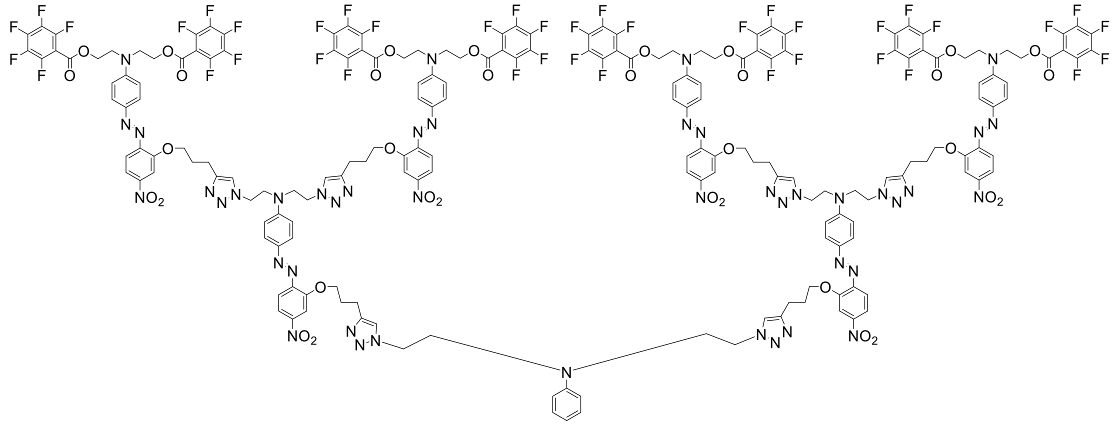


| | $d_{33}$ | PCs | N |
|---|---|---|---|
| C2 | 157 | 5 | 0.470 |
| D-13N | 299 | 13 | 0.569 |

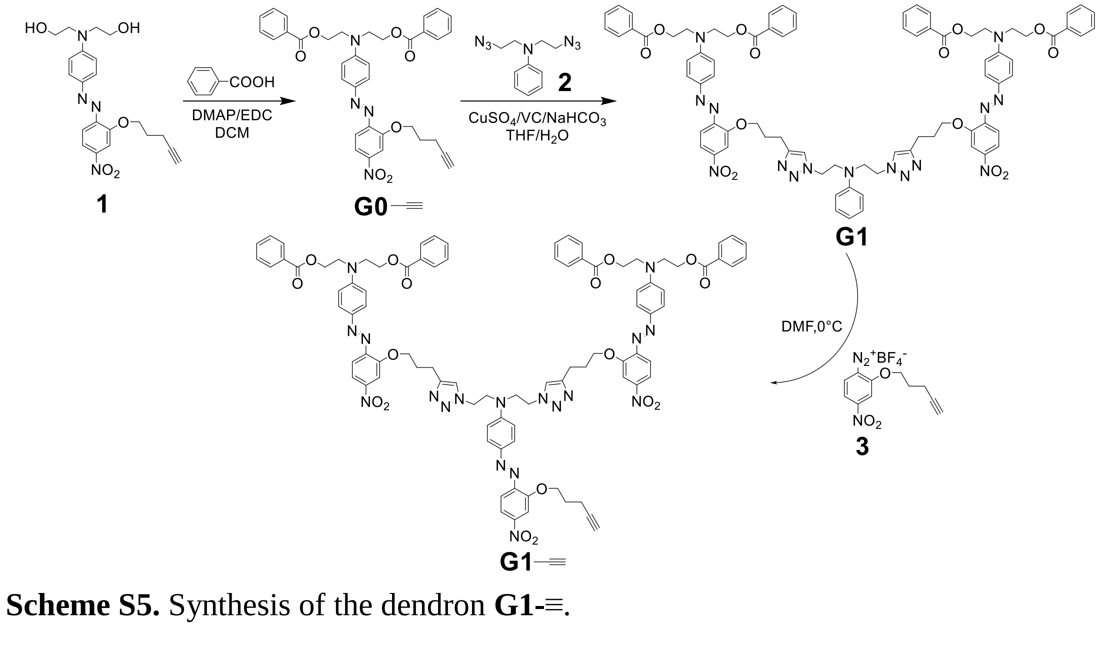
**Scheme S2**. The structures of "X" type dendrimers C2[2], Janus dendrimer D-13N[3] and their related parameters: $d_{33}$ (pm/V); PCs (numbers of containing chromophore moiety pieces); N (%, the loading density of the effective chromophore moieties).



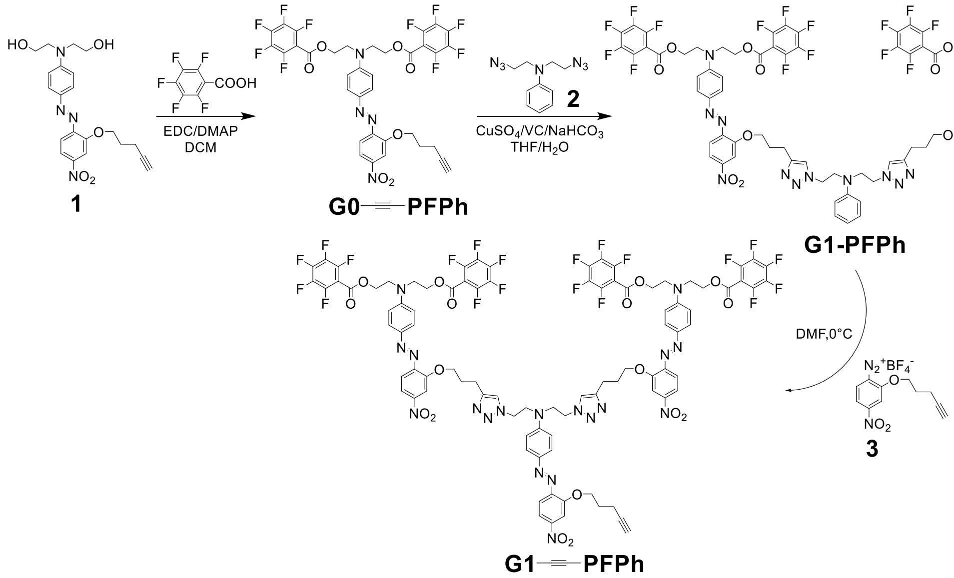
**Scheme S3**. Chemical structure of conical dendrimer **G2**.



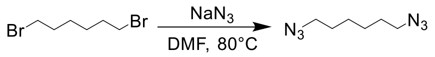
**Scheme S4**. Chemical structure of conical dendrimer **G2-PFPh**.



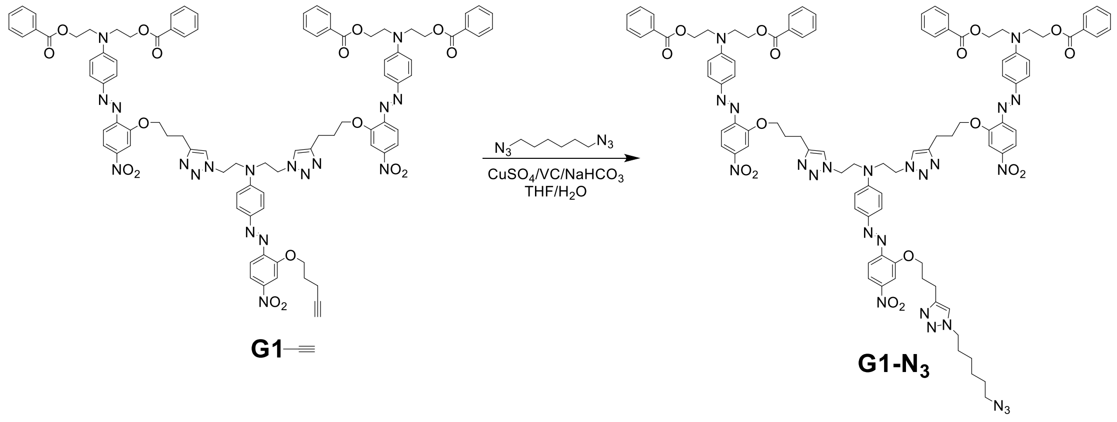
**Scheme S5.** Synthesis of the dendron **G1-≡**.



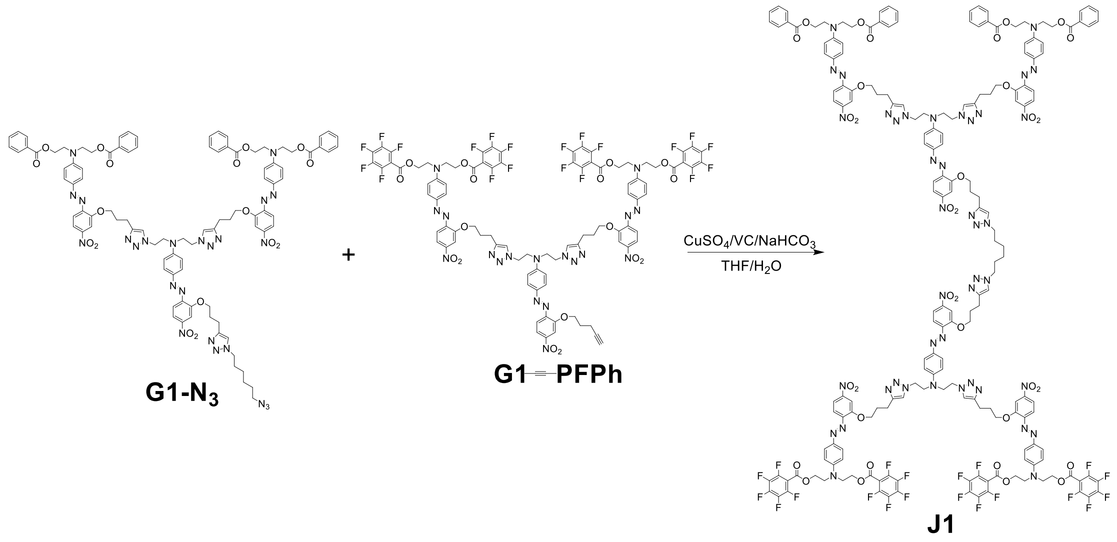
**Scheme S6.** Synthesis of the dendron **G1-≡-PFPh**.



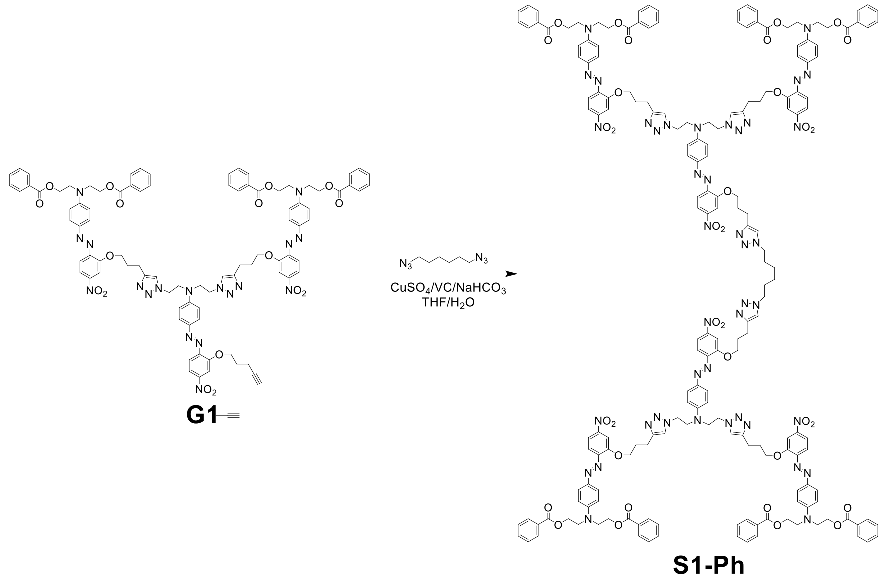
**Scheme S7.** Synthetic route to **1,6-Diazidohexane**.



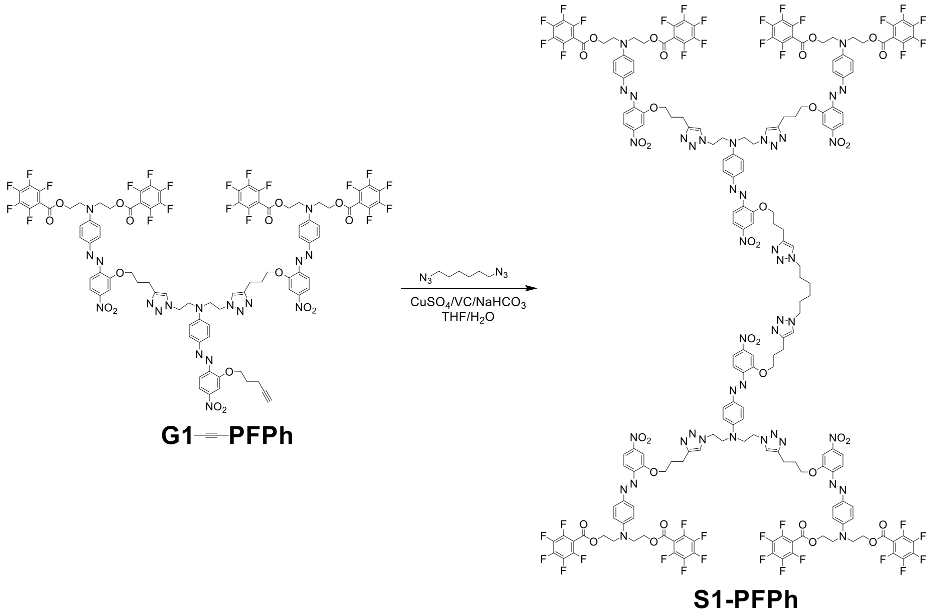
**Scheme S8.** Synthetic route to **G1-N$_3$**.



**Scheme S9.** Synthetic route to dendrimer **J1**.



**Scheme S10.** Synthetic route to dendrimer **S1-Ph**.



**Scheme S11.** Synthetic route to dendrimer **S1-PFPh**.

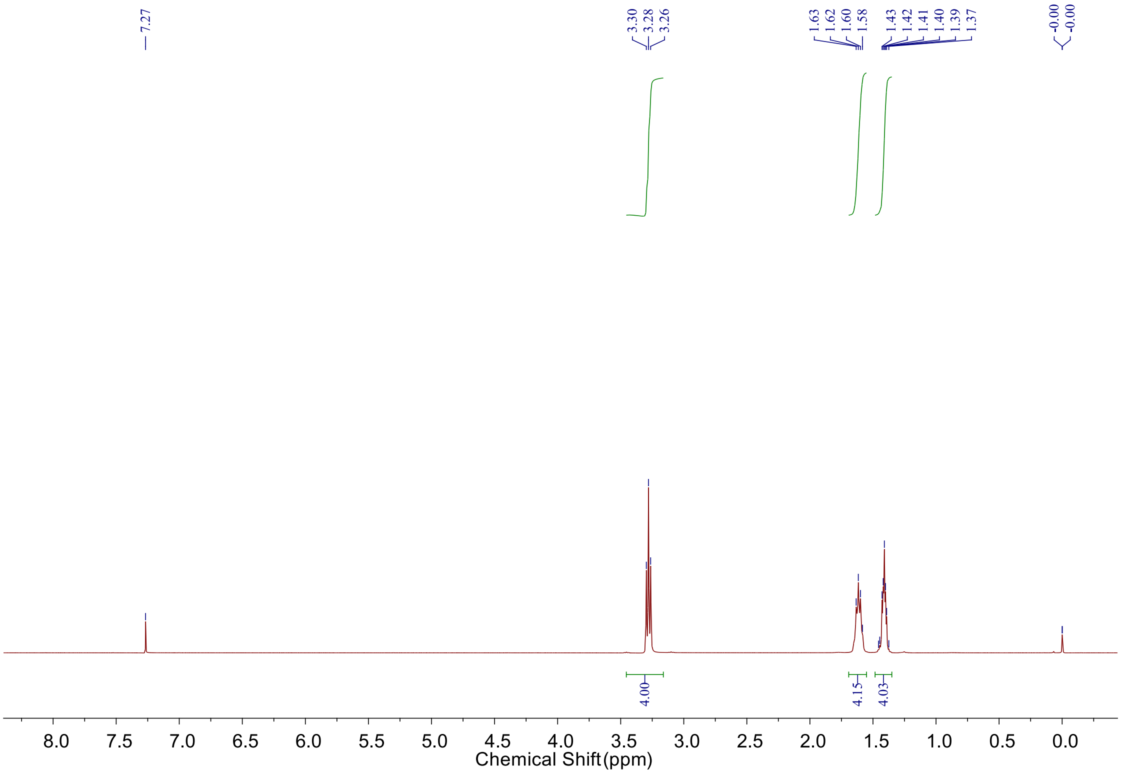


**Fig. S1** $^{1}$H NMR spectrum of **1,6-Diazidohexane** in chloroform-*d*.

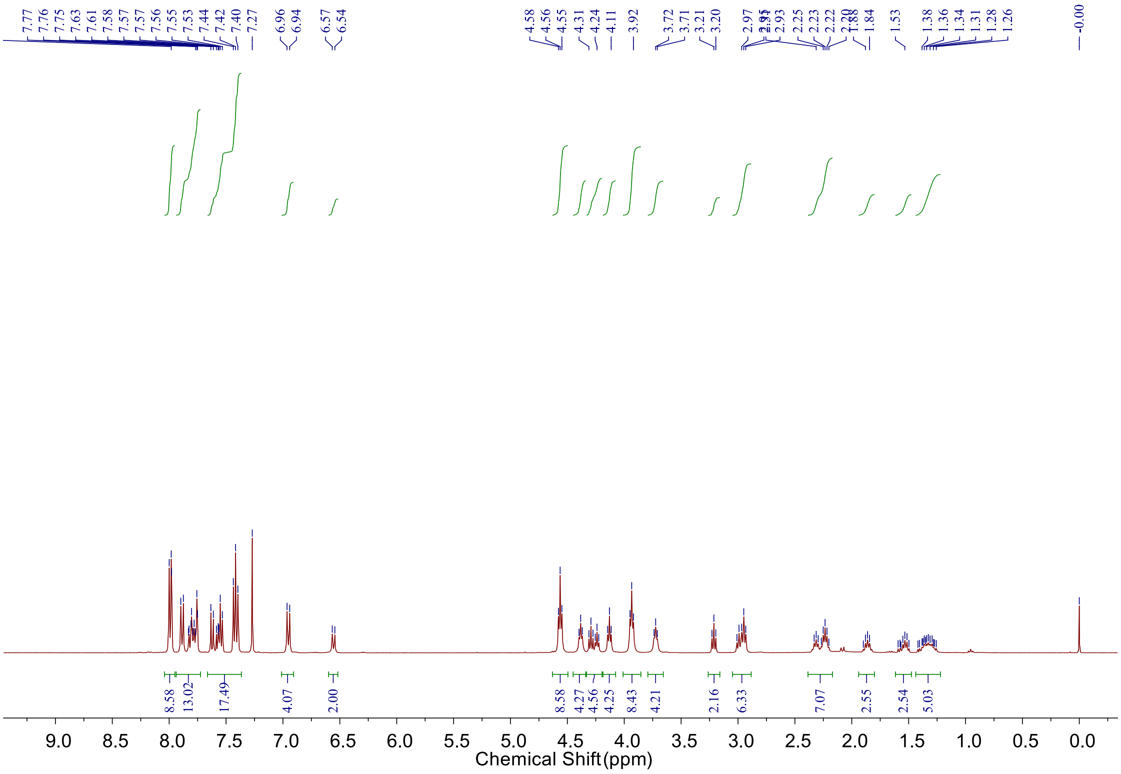


**Fig. S2** $^{1}$H NMR spectrum of **G1-N$_3$** in chloroform-*d*.

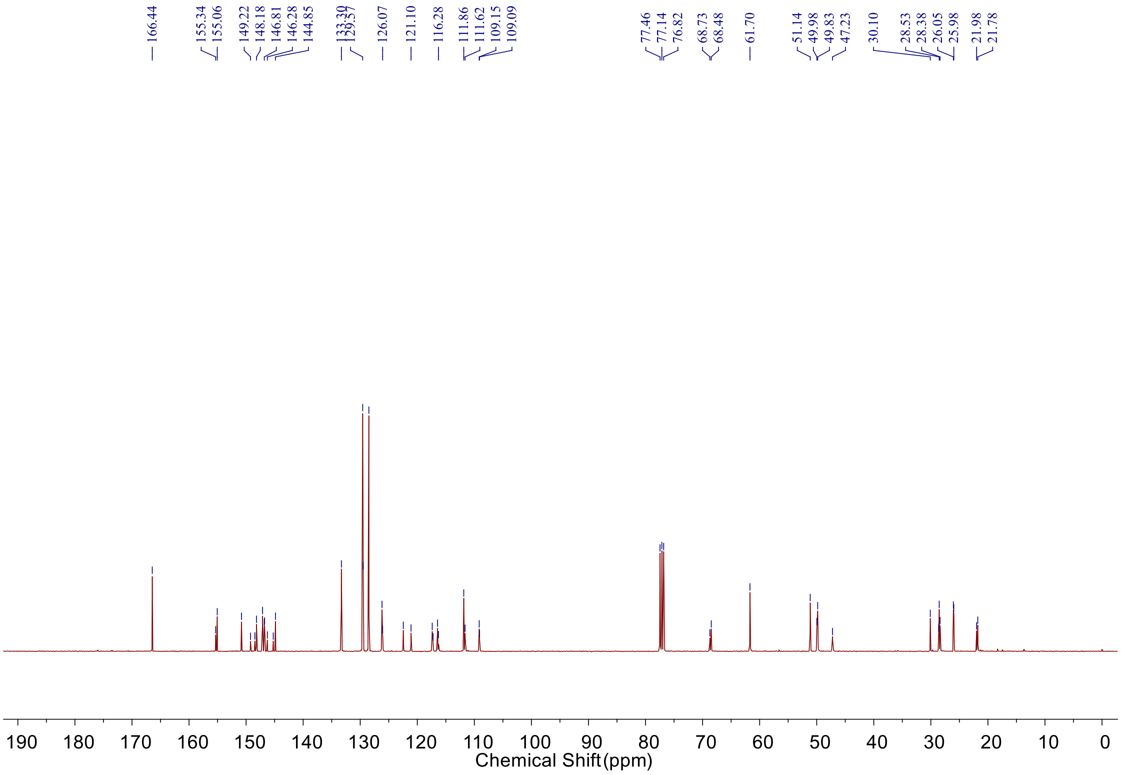


**Fig. S3** $^{13}$C NMR spectrum of **G1-N$_3$** in chloroform-*d*.

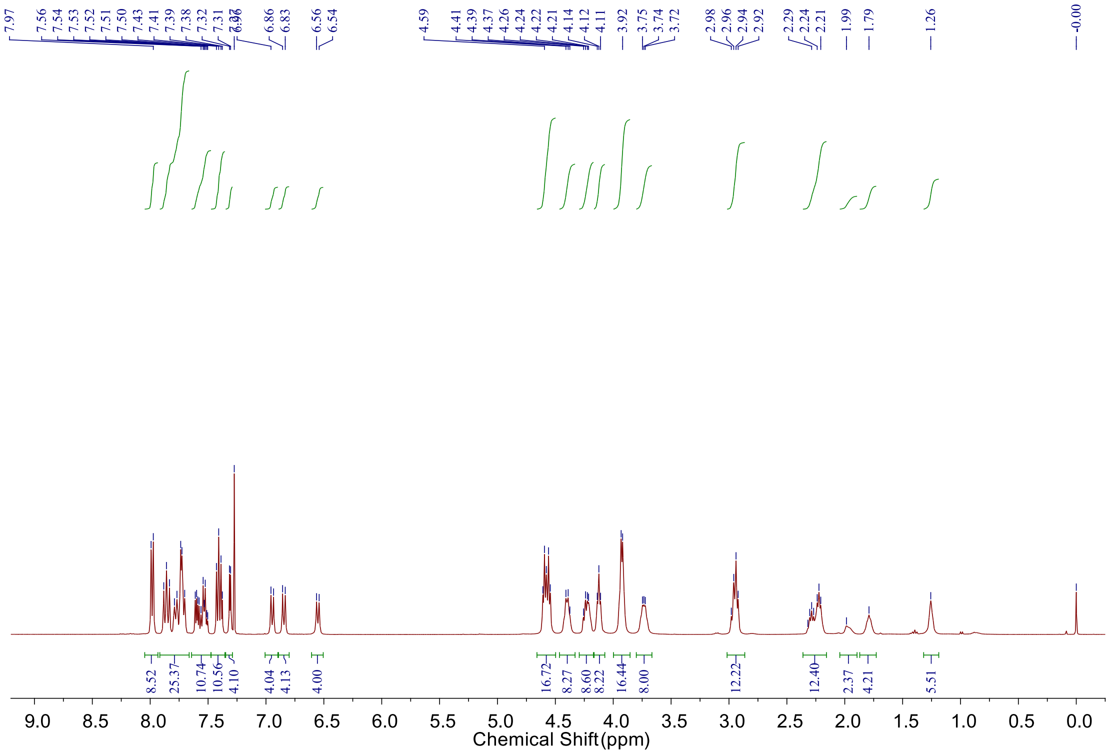


**Fig. S4** $^{1}$H NMR spectrum of **J1** in chloroform-*d*.

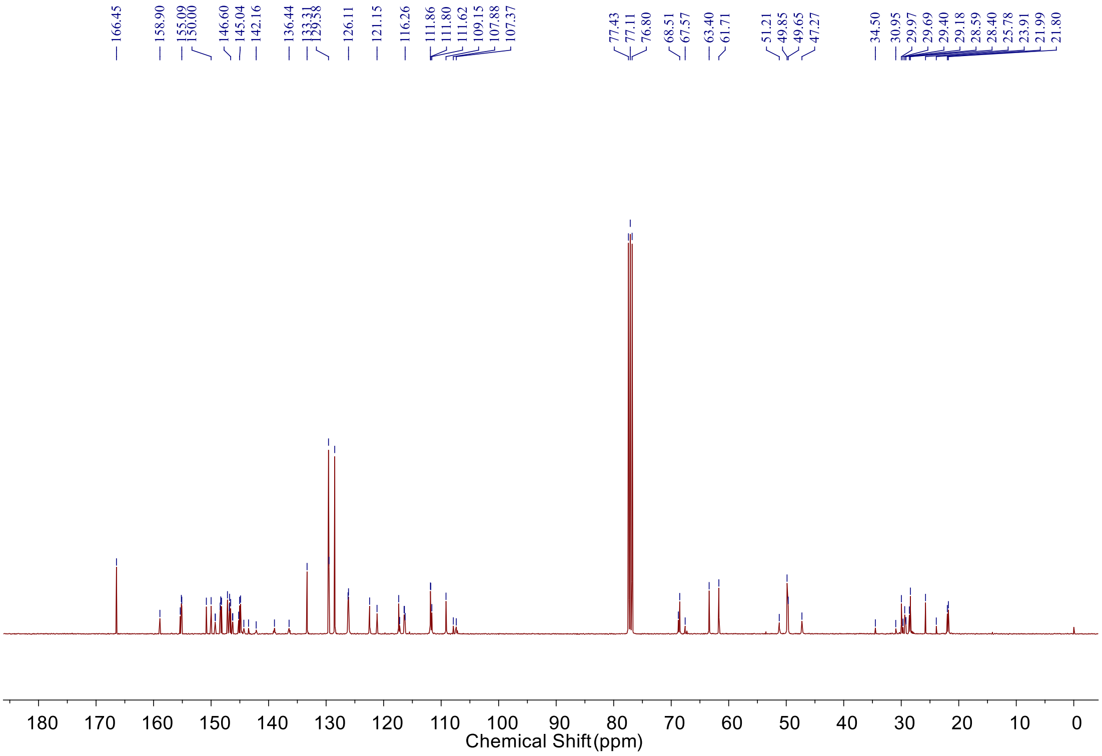


**Fig. S5** $^{13}$C NMR spectrum of **J1** in chloroform-*d*.

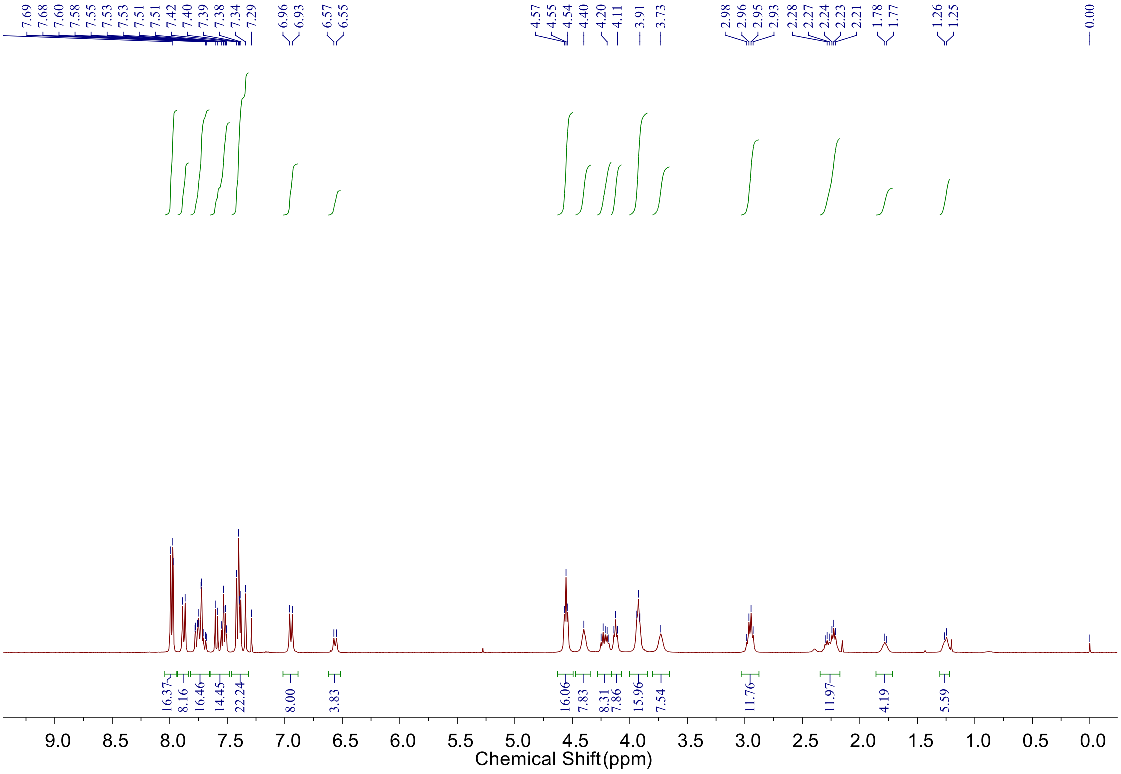


**Fig. S6** $^{1}$H NMR spectrum of **S1-Ph** in chloroform-*d*.

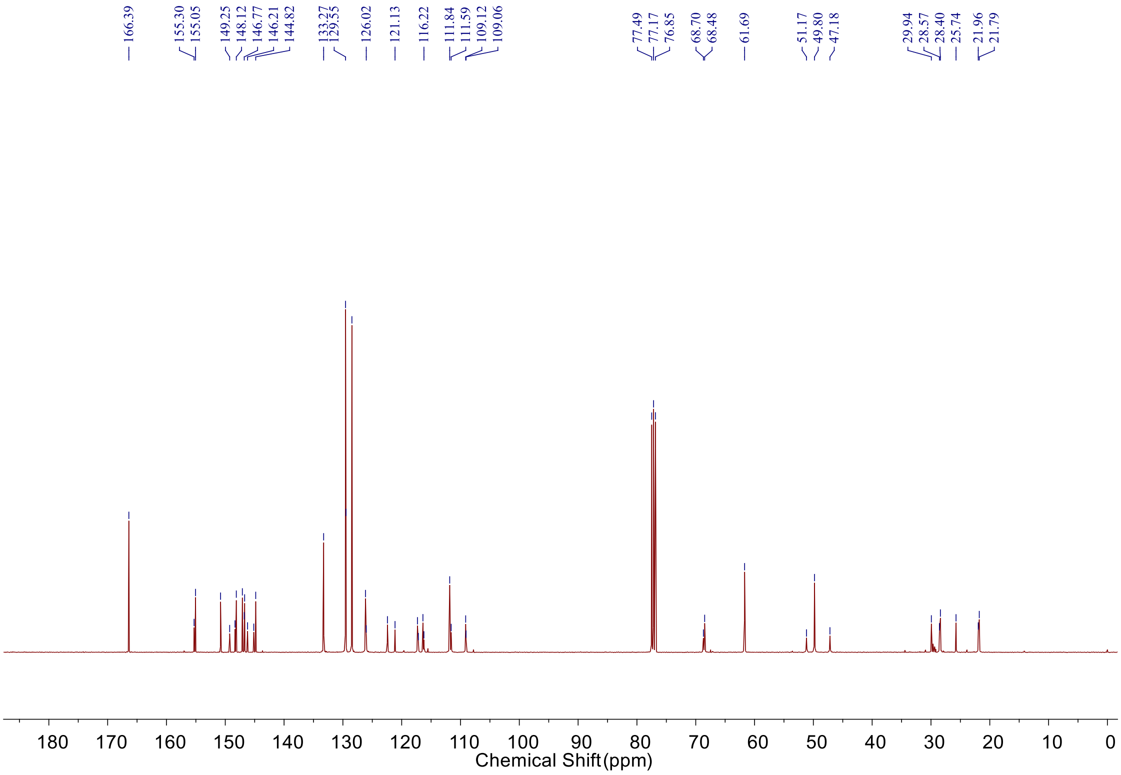


**Fig. S7** $^{13}$C NMR spectrum of **S1-Ph** in chloroform-*d*.

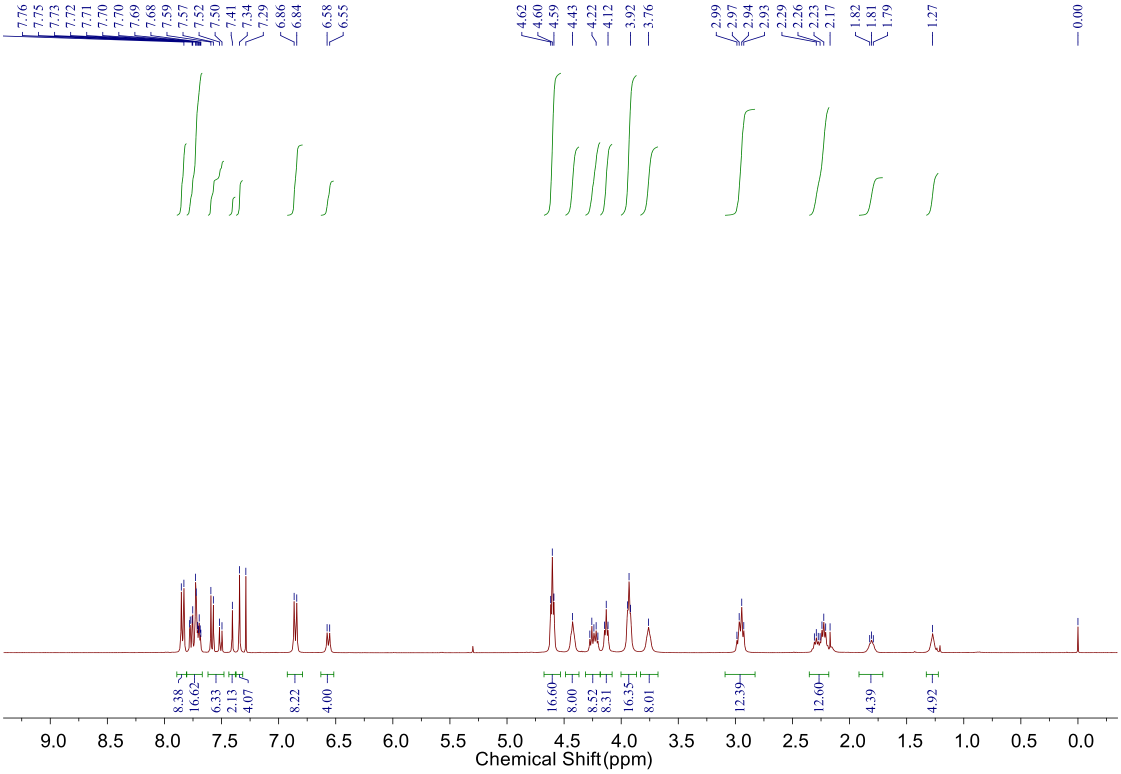


**Fig. S8** $^{1}$H NMR spectrum of **S1-PFPh** in chloroform-*d*.

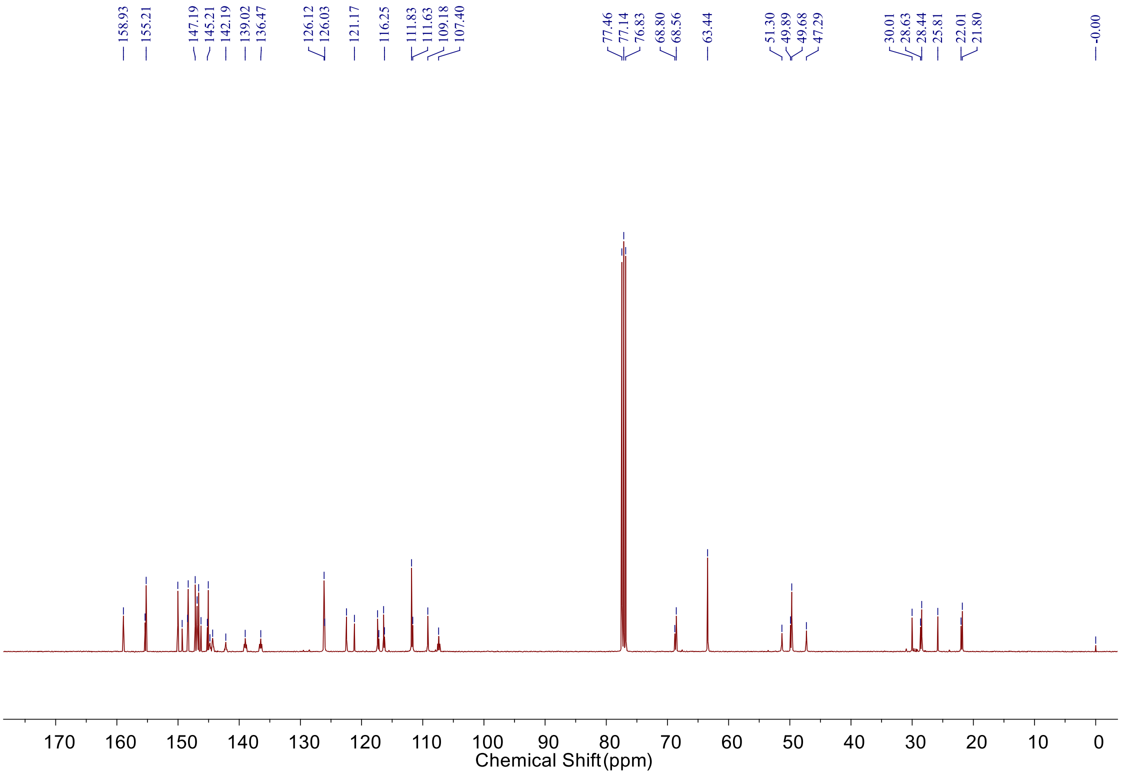


**Fig. S9** $^{13}$C NMR spectrum of **S1-PFPh** in chloroform-*d*.

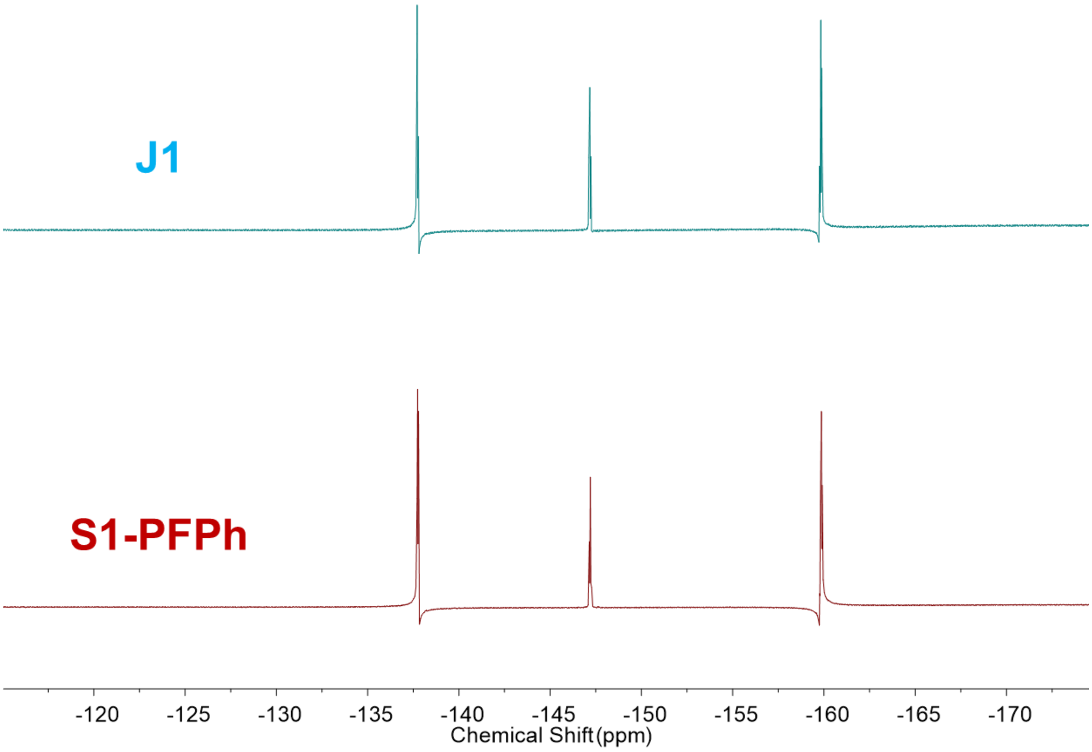


**Fig. S10** $^{19}$F NMR spectra of **J1** and **S1-PFPh**.

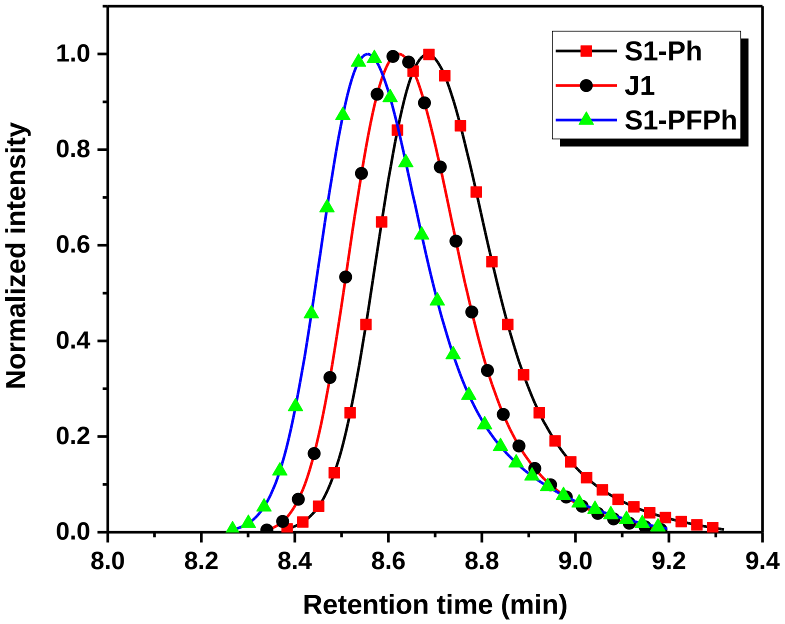


**Fig. S11** GPC curves of dendrimers.

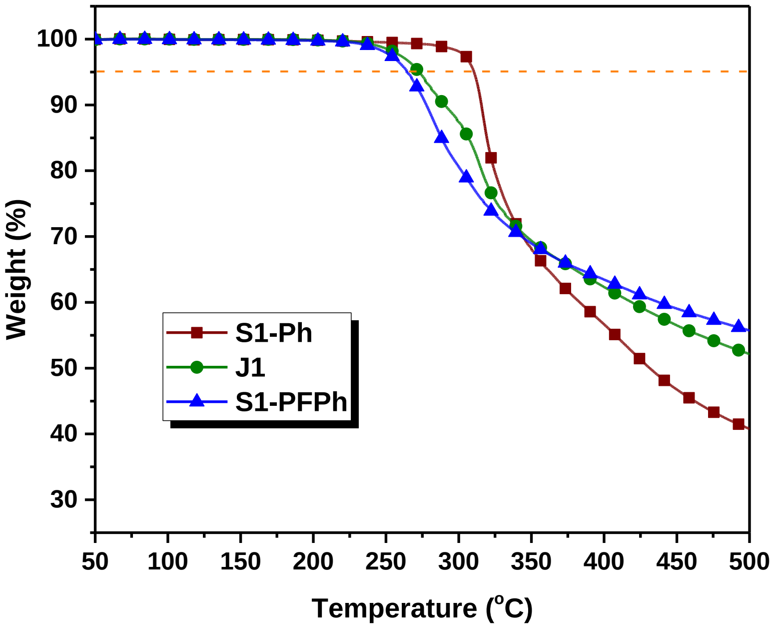


**Fig. S12** TGA thermograms of dendrimers measured in nitrogen at a heating rate of 20 ℃/min.

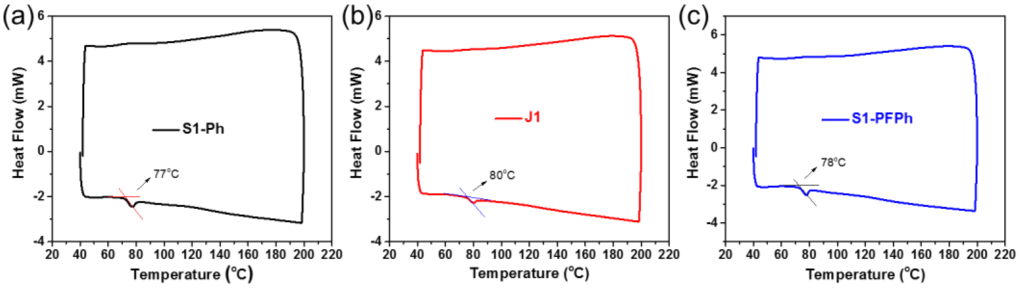


**Fig. S13** DSC curves of dendrimers.

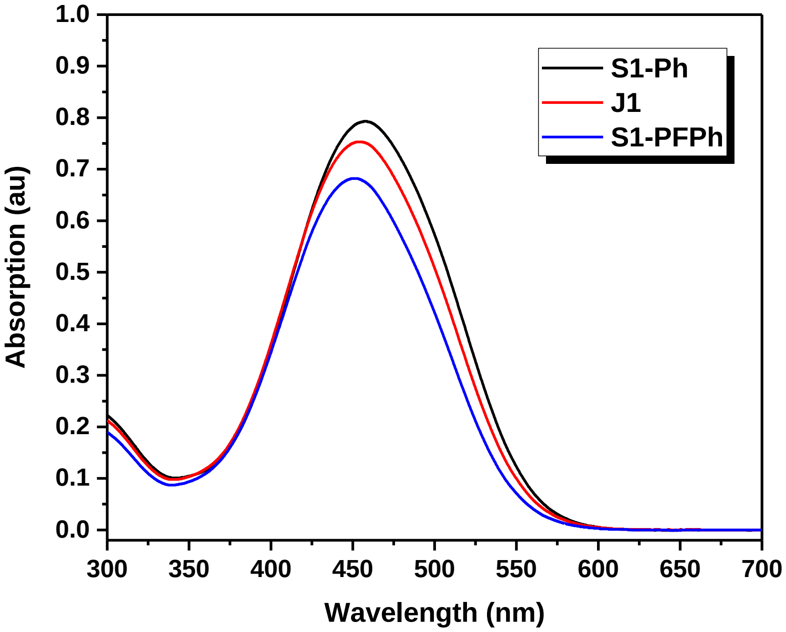


**Fig. S14** UV-Vis spectra of Dendrimers in 1,4-Dioxane solutions.

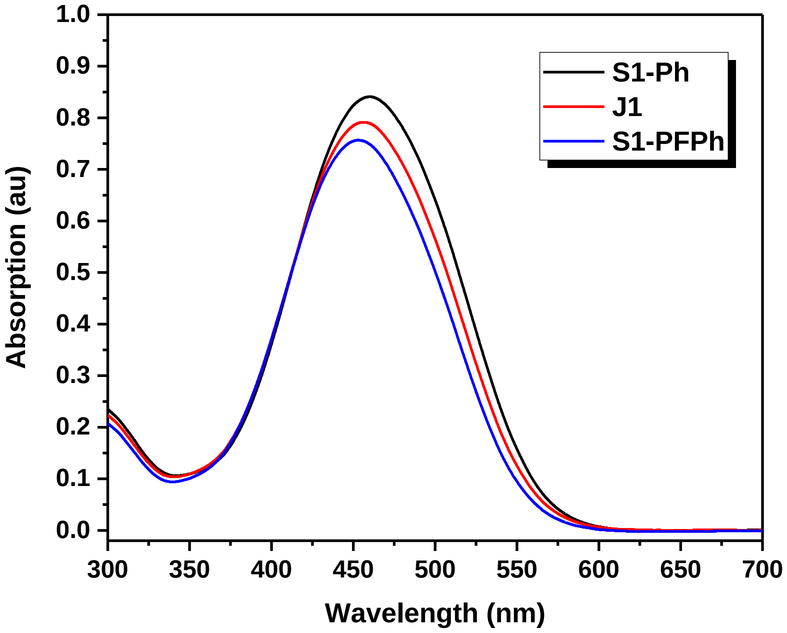


**Fig. S15** UV-Vis spectra of Dendrimers in dichloromethane solutions.

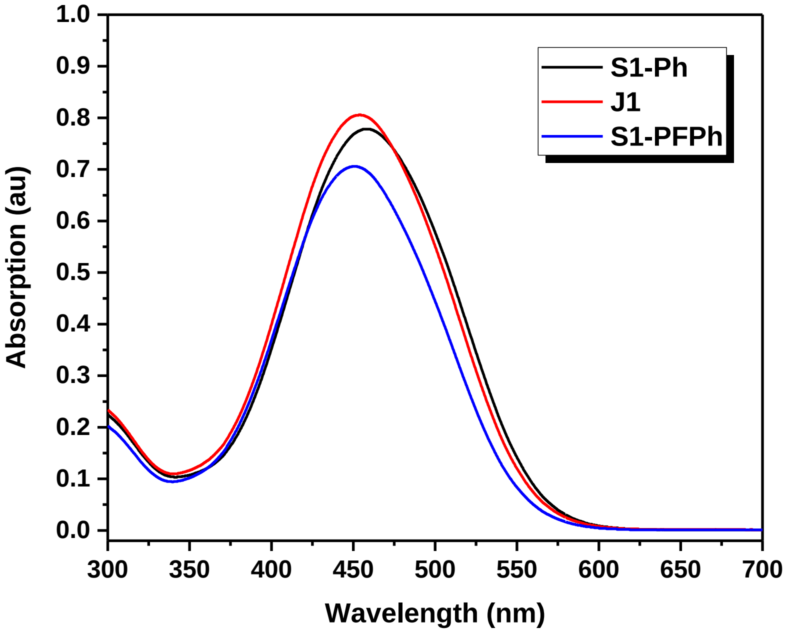


**Fig. S16** UV-Vis spectra of Dendrimers in chloroform solutions.

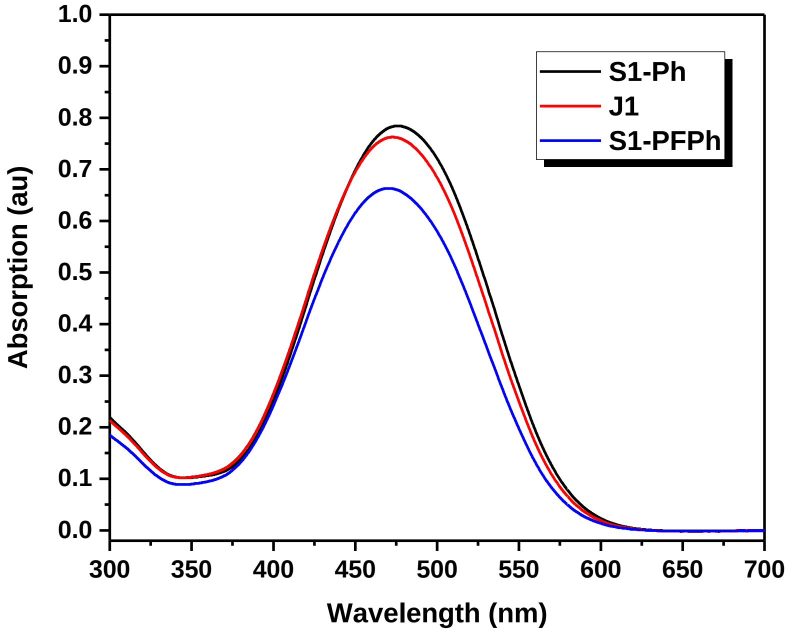


**Fig. S17** UV-Vis spectra of Dendrimers in DMF solutions.

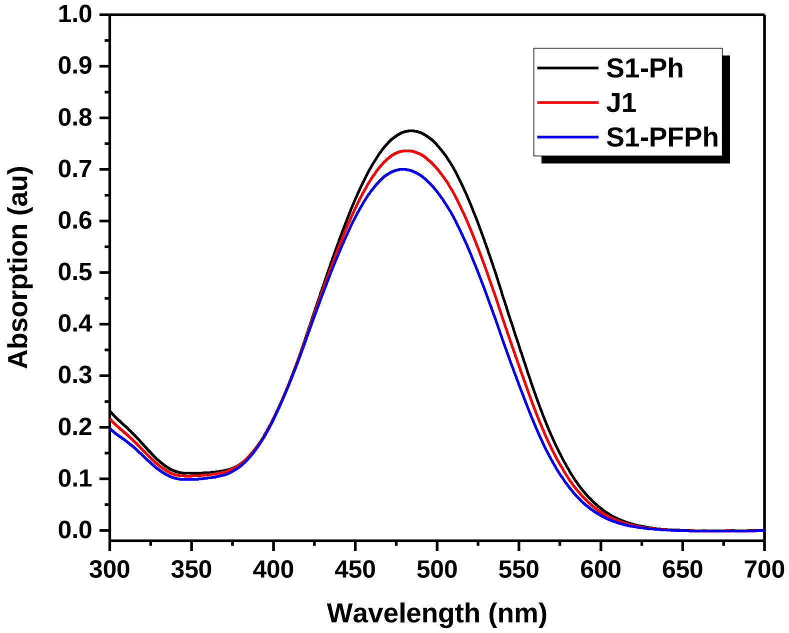


**Fig. S18** UV-Vis spectra of Dendrimers in DMSO solutions.

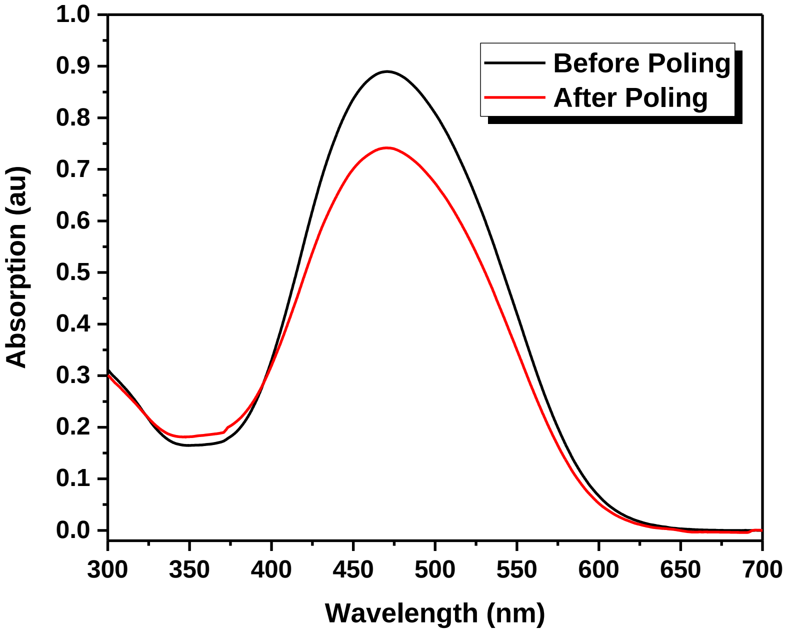


**Fig. S19** UV-vis spectra of the film of **S1-Ph** before and after poling.

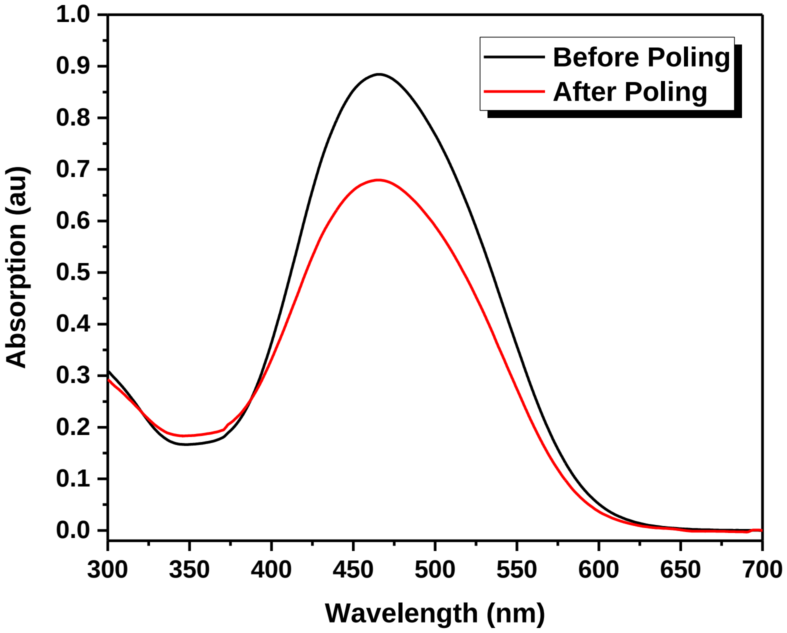


**Fig. S20** UV-vis spectra of the film of **J1** before and after poling.

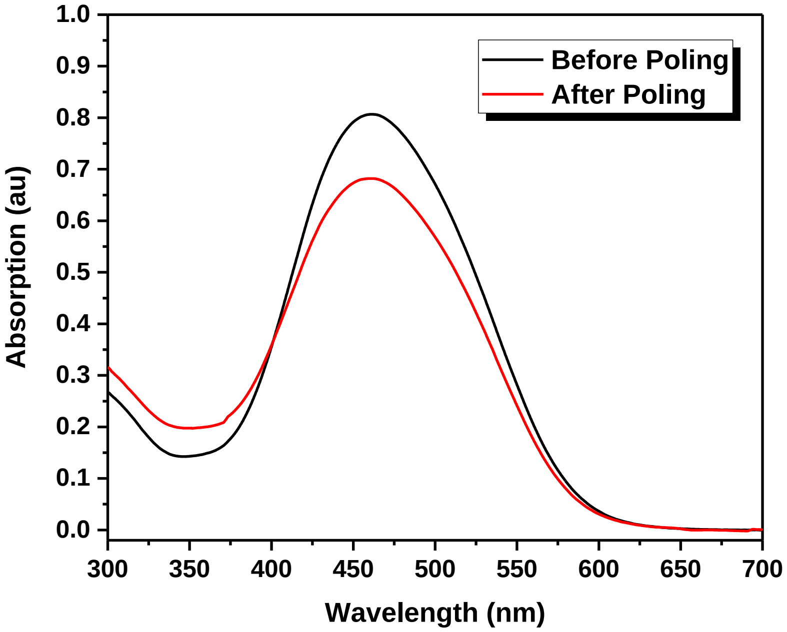


**Fig. S21** UV-vis spectra of the film of **S1-PFPh** before and after poling.

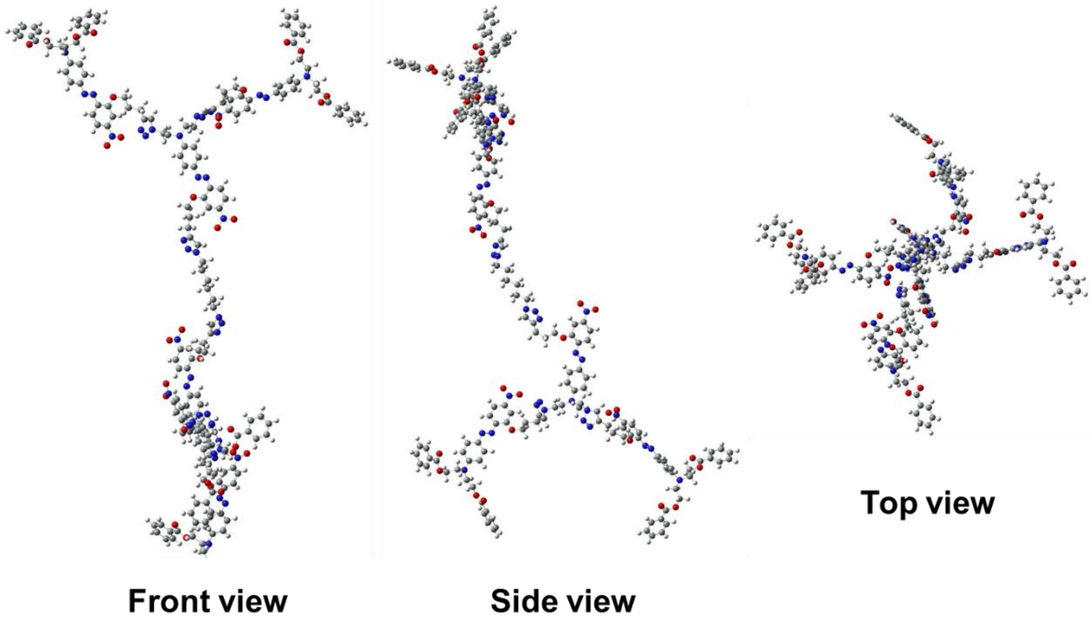


**Fig. S22** The optimized structure of **S1-Ph** viewed from different angles. The configurations of all moleculars were calculated by using the molecular mechanics (MM) simulations with UFF force field in vacuum. The quantum chemical calculations were performed in Gaussian 09 program package.

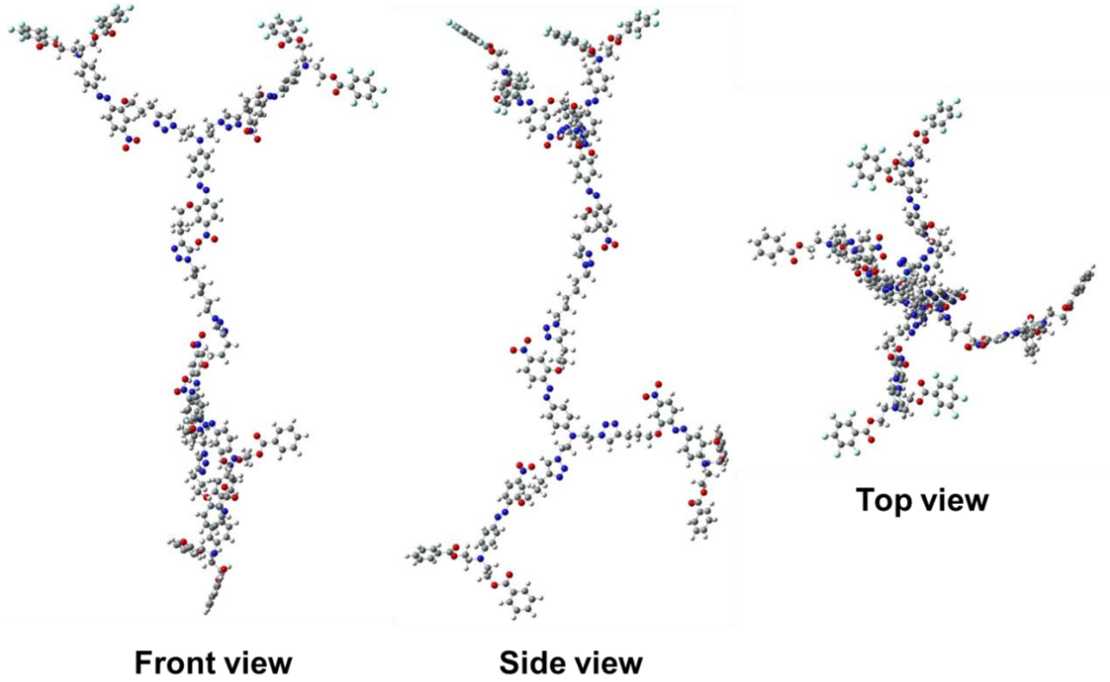

Front view
Side view
Top view

**Fig. S23** The optimized structure of **J1** viewed from different angles.

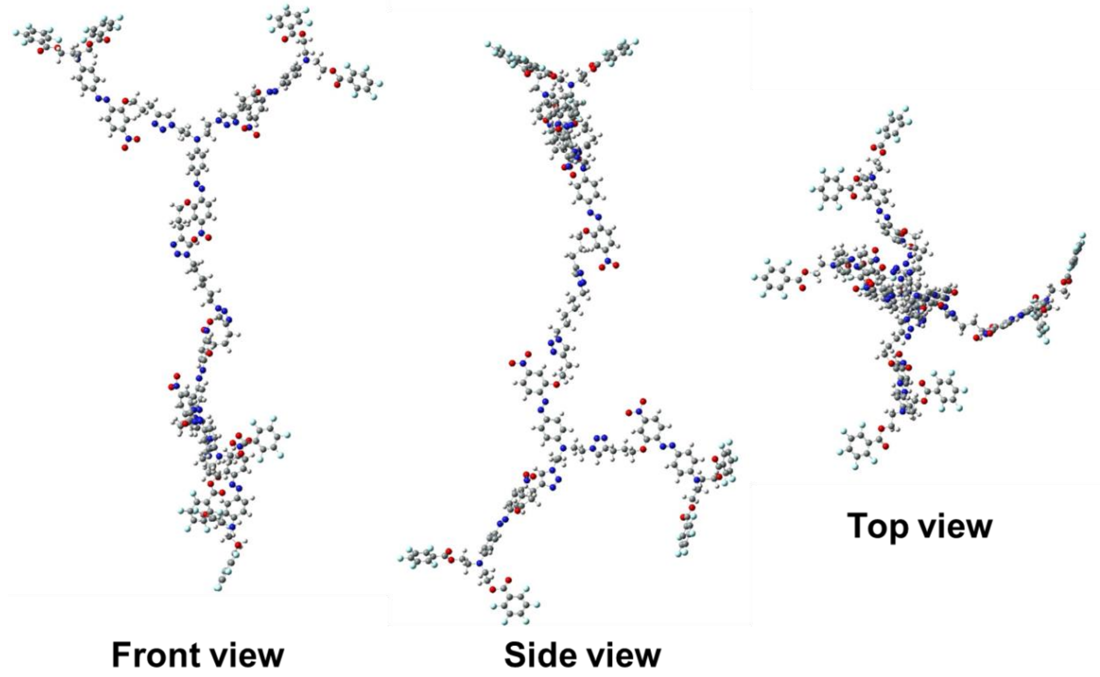

Front view
Side view
Top view

**Fig. S24** The optimized structure of **S1-PFPh** viewed from different angles.

## References

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5. W. Wu, L. Huang, C. Song, G. Yu, C. Ye, Y. Liu, J. Qin, Q. Li and Z. Li, *Chem. Sci.*, 2012, **3**, 1256.