Chinese Chemical Letters 32 (2021) 371–374

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Communication

Guest induced morphology transitions of star shaped pillar[5]arene trimer *via* endo host-guest and “exo-wall” electron-transfer interactions

Wajahat Ali[a], Weitao Gong[a,*], Mehdi Hassan[b], Weidong Qu[a], Lu Liu[a], Guiling Ning[a,*]

[a] State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China
[b] Department of Chemistry University of Baltistan, Skardu, Pakistan

ARTICLE INFO

Article history:
Received 16 January 2020
Received in revised form 3 March 2020
Accepted 16 March 2020
Available online 19 March 2020

Keywords:
Pillar[5]arene
Supramolecular polymers
Host-guest interactions

ABSTRACT

Star shape bridged pillar[5]arene trimer (**C3-PLT**) based on benzene-1,3,5-tricarboxamide (BTAs) was successfully synthesized, which exhibited outstanding guest responsive morphology transition properties. The morphology tuning studies was efficiently achieved with the addition of competitive guest molecules **G1** and **G2** by various self-assembly mechanisms. **C3-PLT** itself displays nanofiber morphology through H-type π-π stacking, and this nanofiber morphology can be completely transformed into spherical vesicles by host-guest interaction **G1,** while upon addition of **G2** into **C3-PLT** by means of “exo-wall” electron-transfer interactions, sheet superstructures can be observed. SEM, ^{1}H NMR, DOSY, fluorescence spectroscopy, and viscosity have verified the formation of supramolecular polymers and morphological transitions between **C3-PLT** with both guests.

Supramolecular self-assembly has gained tremendous attention because it offers adistinctive way to construct various functional supramolecular polymers with futuristic applications in the area of environmental sciences, biomedical sciences, and nanodevices [1,2]. The supramolecular self-assembly can be controlled or transformed by various parameters, including environmental stimuli such as pH, temperature, redox, ions, and light stimuli, polymer concentration, solvent, copolymer composition, hydrophilic fraction [3–8]. Although several kinds of supramolecular polymers with different morphologies have been documented in past few decades, the controlled supramolecular architectures having divergent distinct morphologies such as micelles, vesicles, tubes, and lamellae always remain a prim focus and burning issue in the scientific communal due to the significant potential [9–15]. These architectures exhibit unique and prospective applications in the field of material science, chemical science, biomedicine, biocatalysis, and electronic devices due to their variation in self-assembly and functional characteristics [16–18]. However, in recent literature, most of the morphology transition research has been reported by using external stimuli, *e.g.*, by using different solvents, and introducing responsive moieties into the structure [19,20]. Yao *et al.* reported vesicles and nanofiber morphological transformations through ultrasound reversible heat [21,22]. UV irradiation based structural transformation was revealed by Kim and co-workers [23]. Similarly, an enzyme triggered transformation from micelle to fiber was published by Ulijn’s group [24,25]. Moreover, Meijer *et al.* have reported solvent dependent multifarious self-assemblies transition of benzene-1,3,5-tricarboxamide based derivatives from coil-to-globule [26]. The first instance of solvent-based morphological transformation in this field has provided by Zhao group’s based on bridged pillar[5]-arene trimer and biviologen guest through host-guest interaction. Further, different morphologies have been efficiently obtained, *i.e.*, vesicular structures (0D), tubular objects (1D), layers (2D), and stacked layers (3D) upon increasing the host-guest concentrations [27]. In contrast, the guest-induced morphological transitions of supramolecular polymers are still unexplored [28–30]. Therefore herein, we demonstrated morphology transitions of pillar[5]arene trimer **C3-PLT** before and after addition of guest molecules with different self-assembly approaches in $CHCl_3$. Initially, a bridged pillar[5]arene trimer **C3-PLT** was synthesized by incorporating benzene-1,3,5-tricarboxamide (BTAs) into the three identical pillar-[5]arene. However, we found that the pillar[5]arene trimer **C3-PLT** could directly self-assemble into well-defined nanofiber *via* H-type - stacking (Fig. 1i). Interestingly, after addition of **G1** guestinto host **C3-PLT** which showed an incredibly response by morphological transformation from nanofiber to spherical vesicles (Fig. 1ii) due to the encapsulation of **G1** into the cavity of pillar[5]arene trimer **C3-PLT**. This result revealed the formation of the hyperbranched

* Corresponding authors.
E-mail addresses: wtgong@dlut.edu.cn (W. Gong), ninggl@dlut.edu.cn (G. Ning).

https://doi.org/10.1016/j.cclet.2020.03.044

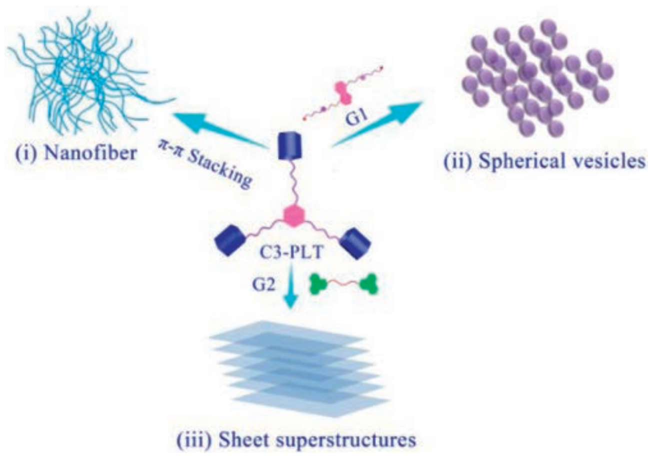

Fig. 1. Graphical presentation of the formation of various morphologies of **C3-PLT** with different guests.

supramolecular polymer through endo host-guest interaction like previously reported hyperbranched supramolecular polymer [31,32].

Furthermore, when the **G2** guest was added into **C3-PLT**, the sheet superstructure morphology was observed (Fig. 1iii) owing to the "exo-wall" interactions *via* π-π stacking between **C3-PLT** host and **G2**. Scanning electron microscopy (SEM) experiments, ^{1}H NMR, 2D DOSY, UV–vis spectroscopy, FL, and viscosity measurements assisted in visualizing the morphology transition from nanofiber to sheet superstructures and host-guest interactions in $CHCl_3$.

Initially, to investigate the self-assembly behavior of **C3-PLT** host,the concentration-dependent UV–vis absorption spectra of **C3-PLT** was carried out in $CHCl_3$ solution shown in (Fig. 2). The **C3-PLT** demonstrates an intensive absorption at 292 nm with 5 μmol/L solution. Upon increasing concentration of host from 5 μmol/L to 200 μmol/L enhancement in intensity, along with 17 nm, blue shift, was observed. This result confirmed the H-type (parallel plane-to-plane stacking) aggregation of **C3-PLT** [33]. Moreover, in order to find more insights about the aggregation behavior of **C3-PLT**, we have examined fluorescence measurement. The fluorescence emission peak of host **C3-PLT** was recorded at 490 nm at 25 °C. When the concentration of **C3-PLT** increases, the fluorescence intensity of **C3-PLT** displayed quenching behavior shown in (Fig. S9 in Supporting information). This fluorescence emission result demonstrated that the presence of π-π stacking in **C3-PLT** host molecules [34].

We reported in our previous work, that the host molecule **C3-PLT** could form super-gel upon irradiation with ultrasound at room temperature and precipitated in acetonitrile by a conventional heating-cooling process [34].

In addition, we acquired a distinct morphology in varying conditions and concentrations through SEM analysis. The acetonitrile-gel produced by sonication showed fibrillar network at 0.2 wt%, and the precipitate obtained from the heating-cooling method showed more rigid and straight rods morphology. Furthermore, concentration-dependent morphologies obtained by altering the concentration of acetonitrile at low concentration the gel self-assemble into pillar-like aggregates when the concentration increased the pillars start to fuse and form a rod-like structure.

Hence this work inspires us, and we envisioned that the host molecule has the ability to change its original morphology when adding appropriate guest molecules.

Therefore, we synthesized two different guests, **G1** and **G2**, to further expand our work and to verify the morphology transition. Additionally, to get a more detailed understanding of the self-assembly process and the morphology transitions of **C3-PLT**, **G1⊂C3-PLT**, and **G2⊂C3-PLT**, SEM was carefully employed to visualize the changes in morphology. The morphology of **C3-PLT** host was studied before and after the addition of guest molecules **G1** and **G2** in $CHCl_3$. The nanofiber morphology was observed for **C3-PLT** host due to the H-type π-π stacking of host molecule itself (Fig. 3a). When **G1** has been added to the host **C3-PLT**, these nanofibers have been completely transformed into vesicles which reveal the formation of hyperbranched supramolecular polymers by means of endo host-guest interaction (Fig. 3b). As a contrast, the sheet superstructures morphology was observed when **G2** was added, due to "exo-wall" interactions between **C3-PLT** and **G2** due to the presence of donor-acceptor electron transfer effect in our system (Fig. 3c).

The host-guest interactions can be readily monitored by fluorescence spectroscopy, so the formation of the host-guest complex between **G1** with **C3-PLT** host in $CHCl_3$ solution was characterized by fluorescence titration (Fig. 4). The fluorescence intensity was increased, and the emission wavelength showed a blue shift (~65 nm) owing to the encapsulation **G1** into the cavity of the **C3-PLT** host. Similarly, fluorescence titration between **C3-PLT** host and **G2** was also carried out in $CHCl_3$ to confirm the electron-transfer interactions. The highly quenching fluorescence spectra were obtained due to the presence of efficient donor-acceptor effect among **C3-PLT** host and **G2**.

To provide further important insights into the host-guest complexation behavior between **C3-PLT** host and **G1**, the concentration-dependent ^{1}H NMR experiment was performed. These experiments were performed upon mixing **G1** and **C3-PLT** at 1:2 ratio from 0.25 mmol/L to 80 mmol/L concentrations in $CDCl_3$. As the concentration of the complex **G1⊂C3-PLT** increased, the relative intensity of 6 peaks of corresponding **G1**, Hi, Hii, Hiii, Hiv showed slight upfield shifting, even shifting towards the negative region indicating that the cyanoalkyl groups of **G1**, were encapsulated into the cavity of **C3-PLT** to form host-guest

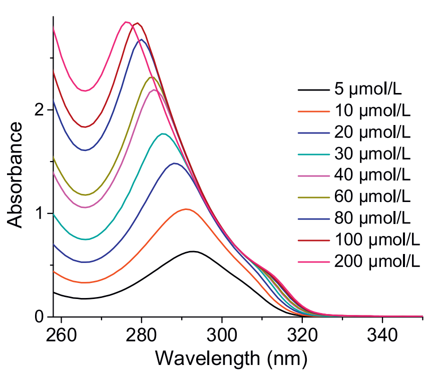

Fig. 2. UV–vis absorption spectra of **C3-PLT** host in $CHCl_3$ solution at different concentrations.

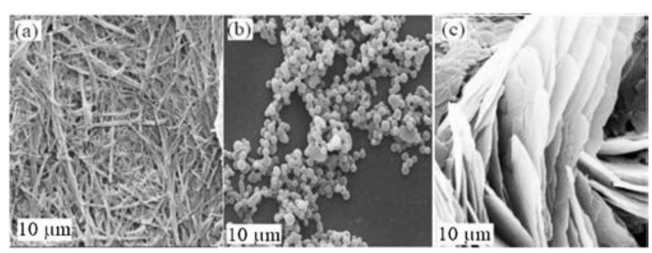

Fig. 3. SEM Morphology transition studies of (a) **C3-PLT** Host, (b) **G1⊂C3-PLT** and (c) **G2⊂C3-PLT** in $CHCl_3$.

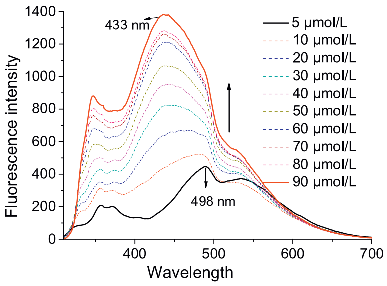

Fig. 4. Emission spectra of **G1⊂C3-PLT** in $CHCl_3$ solution at different concentrations.

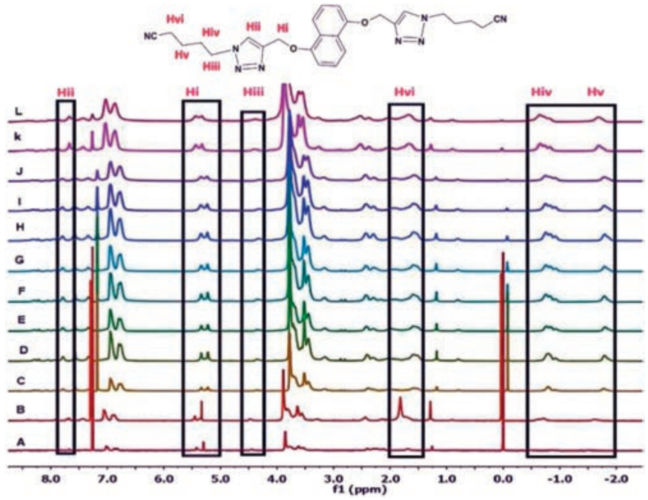

Fig. 5. Concentration dependent [1]H NMR spectra (400 MHz, $CDCl_3$) of **G1⊂C3-PLT** Host at different concentrations: from (A) 2.5 mmol/L to (L) 80 mmol/L.

complexation (Fig. 5). Moreover, all the signals gradually became broad with the increase in concentration which is the indication of the formation of supramolecular polymer. Host at different concentrations showed "exo-wall" interactions.

Similarly, the concentration-dependent [1]H NMR measurements between **C3-PLT** host and **G2** were also recorded to confirm the presence of the "exo-wall" electron-transfer interactions (Fig. 6 and Fig. S10 in Supporting information). The protons signal of **G2**, Hi, Hii and Hiii showed obvious upfield shifts while the proton related to **C3-PLT** Ha, Hb, and Hc showed downfield shifts, suggesting that naphthalene diimide **G2** was not threaded into the cavity of pillar[5]arene. This result verified the presence of "exo-wall" electron transfer interactions between electron-rich **C3-PLT** and electron-deficient **G2**. To further verify the donor-acceptor interactions between **C3-PLT** and **G2**, UV–vis titration was performed in $CHCl_3$. We observed that a new and broad absorption band appeared with an absorption maxima at 420−435 nm in **G2⊂C3-PLT** complex, which was not found separately in the spectrum of either **C3-PLT** host or **G2** (Fig. 7). This outcome revealed the occurrence of the efficient charge-transfer interactions between **C3-PLT** and **G2**. All these results indicated that the presence of two kinds of noncovalent interactions in our system, endo host-guest interactions between **C3-PLT** and **G1**, and "exo-wall" interactions between **C3-PLT** and **G2** by donor-acceptor interactions.

Viscosity is an important and direct index for supramolecular polymerization to provide direct physical evidence for the formation of a non-covalent supramolecular polymer. The micro-Ubbellohde viscometer was used to measure the specific

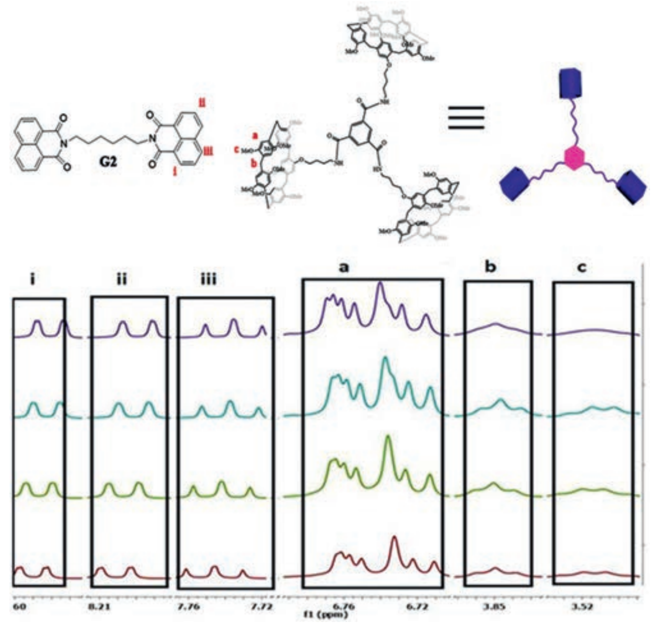

Fig. 6. Concentration dependent [1]H NMR spectra (400 MHz, $CDCl_3$, 298 K) of **G2⊂C3-PLT**.

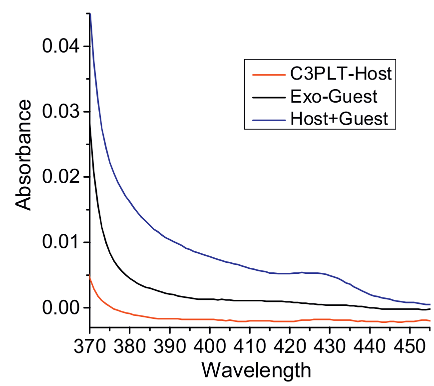

Fig. 7. UV–vis spectra showing CT adsorption band at (420 nm–450 nm) of 2 mmol/L at 1:1 mixture in $CHCl_3$.

viscosity of the equimolar mixture of **G1⊂C3-PLT** and **G2⊂C3-PLT** at 1:2 molar ratio in $CHCl_3$ solution (Fig. 8).

A double logarithmic representation of specific viscosity *versus* the concentration of **G1⊂C3-PLT** and **G2⊂C3-PLT** in $CHCl_3$ was obtained. In the low concentration region, the slope of the curve was 0.72, 0.70, respectively, which is a characteristic for non-interacting assemblies of constant size, indicating the predominance of cyclic oligomers in dilute solution.

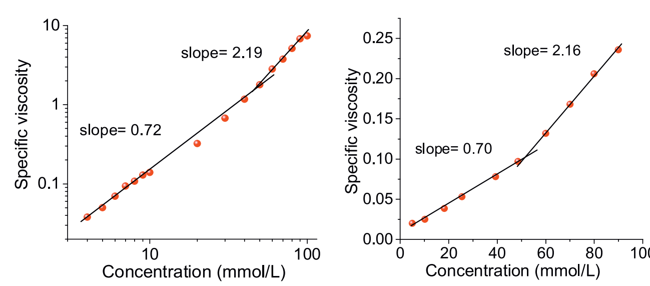

Fig. 8. Specific viscosity measurements of **G1⊂C3-PLT** (left) and **G2⊂C3-PLT** (right).

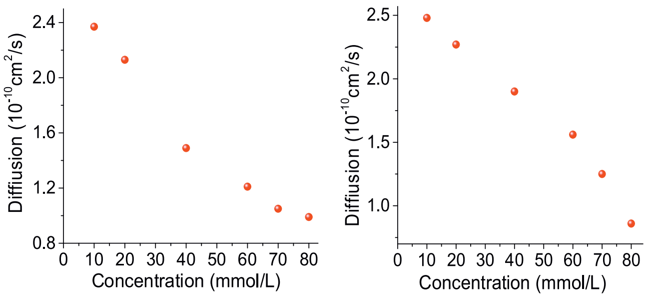

Fig. 9. Concentration dependent DOSY (400 MHz, 298 K) plot of **G1⊂C3-PLT** (left) and **G2⊂C3-PLT** in $CDCl_3$ (right).

When the concentration was increased above (48.90 mmol/L, 50.91 mmol/L respectively), a sharp increase in the viscosity with remarkable increment in the slope value for both **G1⊂C3-PLT** (slope = 2.19) and **G2⊂C3-PLT** (slope = 2.16) was observed indicating a transition from small cyclic oligomers to more prominent supramolecular polymers.

In order to provide further evidence for the construction of supramolecular polymer with high-molecular weight aggregates two-dimensional diffusion-ordered ^{1}H NMR spectroscopy (DOSY) was conducted (Fig. 9). A plot of diffusion coefficient against concentration shows that as the concentration of **G1⊂C3-PLT** and **G2⊂C3-PLT** increased from 2.4 mmol/L to 80 mmol/L, the measured weight-average diffusion coefficient (D) of **G1⊂C3-PLT** and **G2⊂C3-PLT** decreased remarkably from 2.3×10^{-10} m^2/s, 2.3×10^{-10} m^2/s to 0.9×10^{-10} m^2/s. These results showed that larger polymeric structures gradually formed from small oligomers to large-sized supramolecular polymers, which were inherently concentration-dependent.

In conclusion, a star-shape benzene-1,3,5-tricarboxamide (BTAs) bridged pillar[5]arene trimer **C3-PLT** host was successfully synthesized and shows outstanding guest responsive morphology transition properties. The **C3-PLT** host trimer shows nanofiber morphology *via* H-type π-π stacking and this nanofiber morphology was completely transformed into spherical vesicles *via* host-guest interaction with **G1** and sheet superstructures by "exo wall" electron-transfer interactions with **G2**. Furthermore, both supramolecular self-assemblies can form hyperbranched supramolecular polymers, verified by ^{1}H NMR, DOSY, viscosity, FL, and SEM results. We envisage that this hyperbranched supramolecular with tunable morphologies will have potential applications in drug delivery and biomedical engineering. Further work is still ongoing in our lab.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors are grateful for the financial support from the National Natural Science Foundation of China (No. 21206016), the Fundamental Research Funds for the Central Universities (No. DUT-17LK07) and the Natural Science Foundation of Liaoning Province (No. 2019-MS-046).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2020.03.044.

References

[1] X. Yan, J. Li, Chem. Soc. Rev. 39 (2010) 1877–1890.
[2] X. Zhang, C. Dong, W. Huang, et al., Nanoscale 7 (2015) 16666–16670.
[3] Y. Zhou, D. Yan, Chem. Commun. (2009) 1172–1188.
[4] B.Y. Zhou, W. Huang, J. Liu, X. Zhu, D. Yan, Adv. Mater. 22 (2010) 4567–4590.
[5] Z. Guo, Y. Zhang, W. Huang, Y. Zhou, D. Yan, Macromol. Rapid Commun. 29 (2008) 1746–1751.
[6] W. Dong, Y. Zhou, D. Yan, Y. Liu, Phys. Chem. Chem. Phys. 9 (2007) 1255–1262.
[7] R. Deng, M.J. Derry, C.J. Mable, Y. Ning, S.P. Armes, J. Am. Chem. Soc. 139 (2017) 7616–7623.
[8] Y. Bai, C. Liu, D. Chen, et al., Beilstein J. Org. Chem. 15 (2019) 1925–1932.
[9] D. Mandal, S.K. Mandal, M. Ghosh, P. Kumar, Chem. Eur. J. 21 (2015) 12042–12052.
[10] C. Maity, W.E. Hendriksen, J.H. Van Esch, R. Eelkema, Angew. Chem. Int. Ed. 54 (2015) 998–1001.
[11] A.T. Haedler, K. Kreger, A. Issac, et al., Nature 523 (2015) 196–199.
[12] H. Jin, W. Huang, X. Zhu, Y. Zhou, D. Yan, Chem. Soc. Rev. 41 (2012) 5986–5997.
[13] J. Zhang, P.X. Ma, Angew. Chem. Int. Ed. 48 (2009) 964–968.
[14] V.A. Online, Y. Yao, J. Li, et al., RSC Adv. 4 (2014) 9039–9043.
[15] B.C. Wang, Q. Chen, H. Xu, Z. Wang, X. Zhang, Adv. Mater. 22 (2010) 2553–2555.
[16] P. Moitra, K. Kumar, P. Kondaiah, S. Bhattacharya, Angew. Chem. Int. Ed. 53 (2014) 1113–1117.
[17] S. Fleming, R.V. Ulijn, Chem. Soc. Rev. 43 (2014) 8150–8177.
[18] G. Fichman, E. Gazit, Acta Biomater. 10 (2014) 1671–1682.
[19] Y. Wang, N. Ma, Z. Wang, X. Zhang, Angew. Chem. Int. Ed. 46 (2007) 2823–2826.
[20] T. Liu, S. Wang, Y. Song, J. Li, H. Yan, Polym. Chem. 8 (2017) 1306–1314.
[21] D. Ke, C. Zhan, A.D.Q. Li, J. Yao, Angew. Chem. Int. Ed. 50 (2011) 3715–3719.
[22] S. Sun, M. Geng, L. Huang, et al., Chem. Commun. 54 (2018) 13006–13009.
[23] K.I. Anderson, R. Saunders, R.V. Ulijn, Biomater. Sci. 3 (2015) 246–249.
[24] G.M. Huurne, M.A.J. Gillissen, A.R.A. Palmans, I.K. Voets, E.W. Meijer, Macromolecules 40 (2015) 3949–3956.
[25] P. Van Der Schoot, E.W. Meijer, A.R.A. Palmans, Chem. Commun. 48 (2012) 3803–3805.
[26] H. Zhang, K.T. Nguyen, X. Ma, et al., Org. Biomol. Chem. 11 (2013) 2070–2074.
[27] T. Ogoshi, S. Kanai, S. Fujinami, T.A. Yamagishi, Y. Nakamoto, J. Am. Chem. Soc. 130 (2008) 5022–5023.
[28] Y. Liu, Y. Zhang, H. Zhu, et al., Mater. Chem. Front. 2 (2018) 1568–1573.
[29] J. Zhang, J. Zhu, C. Lu, et al., Polym. Chem. 7 (2016) 4317–4321.
[30] X. Wang, H. Deng, J. Li, et al., Macromol. Rapid Commun. 34 (2013) 1856–1862.
[31] S. Sarkar, P. Choudhury, S. Dinda, P.K. Das, Langmuir 34 (2018) 10449–10468.
[32] A. Ajayaghosh, C. Vijayakumar, R. Varghese, S.J. George, Angew. Chem. Int. Ed. 45 (2006) 456–460.
[33] L. Brunsveld, J.A.J.M. Vekemans, J.H.K.K. Hirschberg, R.P. Sijbesma, E.W. Meijer, Proc. Natl. Acad. Sci. 99 (2002) 499–4982.
[34] X. Kuang, A. Wajahat, W. Gong, et al., Soft Matter 13 (2017) 4074–4079.