ChemComm

COMMUNICATION



View Article Online View Journal | View Issue

Cite this: Chem. Commun., 2014, 50, 9477

Received 28th April 2014, Accepted 29th May 2014

Construction of supramolecular hyperbranched polymers *via* the "tweezering directed self-assembly" strategy[†]

Yu-Kui Tian,^a Zhi-Shuai Yang,^a Xiao-Qin Lv,^a Ri-Sheng Yao*^b and Feng Wang*^a

DOI: 10.1039/c4cc03158j

www.rsc.org/chemcomm

A bis-alkynylplatinum(III) terpyridine tweezer-alkynylgold(IIII) diphenylpyridine guest is shown to maintain the specific complexation in the presence of a B21C7-secondary ammonium salt recognition motif, which facilitates the formation of supramolecular hyperbranched polymers *via* the "tweezering directed self-assembly" strategy.

The integration of donor and acceptor chromophores in a mixed array is a convenient approach to construct nano-sized optoelectronic devices.¹ Due to the non-specific and non-directional properties of donor-acceptor interactions, a variety of erratic stacking modes (such as phase segregation, random or alternating mixing) could exist,² which is disadvantageous for device performance. In this respect, the precise organization of π -conjugated donor and acceptor moieties *via* supramolecular control is of paramount importance. We have recently developed the "tweezering directed self-assembly" strategy for the construction of well-defined donor-acceptor arrays.3 Considering that the two electron-deficient alkynylplatinum(II) terpyridine pincers on the molecular tweezer unit facilitates the encapsulation of electron-rich guests such as pyrene,⁴ the resulting AB-type monomers could efficiently assemble into linear supramolecular polymers in CHCl₃ solution.³ It is worthy of note that such a strategy overcomes the non-directional complexation problems for the conventional donor-acceptor interactions, thus leading to the exact positioning of alternating donor and acceptor chromophores.

To expand the scope of the "tweezering directed self-assembly" strategy, the compatibility of the tweezer–guest recognition motif should be extensively examined in the presence of other functional groups. Based on this consideration, herein another type of non-covalent recognition motif, namely benzo-21-crown-7

P. R. China. E-mail: drfwang@ustc.edu.cn; Fax: +86 551 6360 6095

^b School of Medical Engineering, Hefei University of Technology, Hefei,

Anhui 230009, P. R. China. E-mail: Rishengyao@163.com † Electronic supplementary information (ESI) available: Synthesis, characteriza-



Supramolecular hyperbranched polymers 5

Scheme 1 Schematic representation of the construction of supramolecular hyperbranched polymers 5.

(B21C7)–secondary ammonium salt moieties,⁵ is implemented and employed as the branching unit for the construction of supramolecular hyperbranched polymers **5** (Scheme 1). Due to the limited solubility of the secondary ammonium salt in CHCl₃, more polar solvent mixtures such as CHCl₃/CH₃CN (2:1, v/v) were required to accomplish the supramolecular polymerization process. Therefore, emphasis should be placed on the tolerance of the tweezer–guest recognition moieties to the modified external conditions.

Our preliminary study revealed that the previously utilized bis-alkynylplatinum(π) terpyridine molecular tweezer-pyrene recognition motif³ is not a desirable candidate for the fabrication of 5, since its binding affinity is rather weak in CHCl₃/CH₃CN (2:1, v/v) solution (manifested by the very slight absorption

^a Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026,

tion, UV-Vis titration data and other materials. See DOI: 10.1039/c4cc03158j

changes in the UV/Vis titration experiments, Fig. S34, ESI†). Therefore, in this communication pyrene was replaced by the alkynylgold(m) diphenylpyridine unit, which has been proven to exhibit enhanced complexation towards the molecular tweezer moiety.^{4*a,b*} Specifically, heteroditopic monomers **1** and **2** were designed (Scheme 1), both of which bear B21C7 units on one side. The bis-alkynylplatinum(m) terpyridine tweezer and alkynylgold(m) diphenylpyridine guest were decorated on the other side. If the highly specific complexation of the tweezer–guest recognition motif is maintained, the mixing of equivalent amounts of **1** and **2** should afford the dimeric complex **4**. Subsequent addition of the homotritopic secondary ammonium salt monomer **3** to **4** was anticipated to furnish the desired A_2B_3 -type supramolecular hyperbranched polymers **5** with stimuli-responsive character.^{6,7}

The synthetic routes towards the desired monomers 1–3 were quite straightforward (Scheme S1–S3, ESI[†]). The purpose of introducing long alkyl chains on 1–3 was to increase the solubility of the self-assembled monomers. In addition, these flexible spacers were expected to decrease the conformational entropy of the multiple non-covalent complexation processes.⁸ The structures of the synthetic compounds were validated by NMR and ESI-MS spectra (Fig. S1–S33, ESI[†]).

The non-covalent complexation was first studied between the monotopic molecular tweezer 6 and alkynylgold(m) diphenylpyridine guest 7 (Scheme 1). When an equivalent amount of 7 was added to 6 in $CDCl_3/CD_3CN$ (2:1, v/v), the originally broad ¹H NMR spectrum of 6 (mainly resulting from the irregular self-complexation of 6, Fig. S4, ESI[†]) converted to well-defined signals (Fig. S35, ESI†), illustrating the preferential sandwiching of 7 into the cavity of 6. The fast-exchanging complexation property of the tweezer-guest binding motif was also confirmed, as demonstrated by the presence of only one set of ¹H NMR signals. Based on the molar ratio plot (Fig. 1a) derived from the ¹H NMR titration experiment (Fig. S35, ESI[†]), the binding stoichiometry between 6 and 7 was determined to be 1:1. Moreover, the tweezer-guest binding affinity could be quantitatively evaluated by UV/Vis spectroscopy, as a result of the fascinating optical properties of the alkynylplatinum(II) terpyridine units on 6. Briefly, the MLCT and LLCT absorption bands of 6 were located predominately between 400 and 500 nm in the UV/Vis spectrum (Fig. 1b,



Fig. 1 (a) Molar ratio plot for monomers **6** and **7** derived from a ¹H NMR titration experiment (monitoring the chemical shift changes of H_a on **7**); (b) change in the UV/Vis absorption spectra at 460 nm upon stepwise addition of gold(III) alkynyl complexes **7** to the molecular tweezer **6**: the red line was obtained from non-linear curve-fitting. Inset: UV/Vis absorption changes at 5.00×10^{-5} M in CHCl₃/CH₃CN (2:1, v/v).

inset).⁴ Upon progressive titration of 7 to 6 in CHCl₃/CH₃CN (2:1, v/v), the intensity of the MLCT-LLCT absorption bands gradually decreased. Non-linear curve-fitting of the UV/Vis absorption data obtained at 460 nm (eqn (S1), ESI⁺) provided the association constant ($K_a = (3.33 \pm 0.39) \times 10^4 \text{ M}^{-1}$) for 6/7 (Fig. 1b). The strong tweezer-guest complexation capability is also supported by the UV/Vis titration experiments for the complexes 6/2 (bearing one B21C7 unit) and 1/2 (bearing two B21C7 units), which gave association constant values of (1.43 \pm 0.61 \times 10⁴ M⁻¹ and (6.66 \pm 1.11) \times 10³ M⁻¹, respectively (Fig. S36 and S37, ESI⁺). Based on the above three calculated values, it is evident that pendant crown ether units exert negative effects on the tweezer-guest binding affinity, which could be ascribed to the following two factors. One is due to the direct encapsulation of the o-dioxybenzene group located on the B21C7 unit in the cavity of the molecular tweezer, whilst another indirect effect arises from the B21C7-induced polarity increase of the microenvironment.9

To pursue more convincing explanations for the B21C7induced decrease of the tweezer–guest binding affinity, we chose monotopic **6**, **7**, the B21C7 ester and a secondary ammonium salt as the model compounds and carried out four-component molecular recognition studies (Fig. S38, ESI†). It is well-known that slow-exchanging B21C7–secondary ammonium salt recognition motif features 1:1 binding stoichiometry.⁵ Hence, after mixing equivalent amounts of the four monotopic compounds together in CDCl₃/CD₃CN (2:1, v/v), the resulting spectrum (Fig. S38a, ESI†) was found to almost overlap the ¹H NMR spectra of the corresponding **6**/7 and B21C7–secondary ammonium salt complexes (Fig. S38b–e, ESI†), supporting the non-interfering complexation model for these two non-covalent recognition motifs.

Besides the above monotopic model system, the designed monomers 1-3 could also demonstrate highly specific complexation behavior via a step-wise self-assembly pathway (Fig. S39, ESI[†]). Practically, after mixing equivalent amounts of 1 and 2 (9 mM for each monomer) together, specific tweezer-guest complexation takes place, as visualized by the significant upfield shift of the H₁₈ signal (from 7.332 to 7.198 ppm). Meanwhile, the signals corresponding to the H₂₀₋₂₂ protons belonging to the B21C7 unit hardly changed, implying that the preferential tweezer-guest complexation occurred without the involvement of the crown ether unit (Fig. S39c, ESI⁺). On this basis, subsequent addition of 3 (6 mM) led to the splitting of protons H_{20-22} belonging to B21C7, suggesting its favorable association with the secondary ammonium salt moiety (Fig. S39b, ESI⁺). Interestingly, unlike the above-mentioned monotopic systems, herein two sets of proton signals were present in the NMR spectrum for the fast-exchanging tweezer-guest moieties (such as H1 and H3), corresponding to the B21C7-complexed and B21C7-uncomplexed species, respectively.

Notably, all of the above NMR experiments give clear evidence that the possibility for the direct complexation of the *o*-dioxybenzene group on B21C7 with the tweezer unit could be totally excluded. Hence, the decreased tweezer–guest binding strength primarily results from the presence of B21C7 ethyleneoxy chains, which increase the polarity of the microenvironment. Consequently, the electropositivity of the alkynylplatinum(II) terpyridine unit could be potentially dispersed, leading to a weakening of the donor-acceptor interactions.

After elucidating the highly specific non-covalent recognition behavior, the supramolecular polymerization process was performed via the "one-pot" mixing of the three monomers 1-3 at different concentrations. As shown in Fig. 2, for the 3:3:2 mixture of 1, 2 and 3 at low monomer concentrations, the ¹H NMR spectra exhibit signal splitting for both the fastexchanging (such as for H_{1,3,5} on the tweezer-guest moieties) and slow-exchanging (such as for H24,25 on the B21C7-secondary ammonium salt moieties) recognition motifs, suggesting the coexistence of supramolecular oligomeric and polymeric species. Increasing the monomer concentration favors the formation of supramolecular hyperbranched polymers, as manifested by the fact that the oligomeric signals progressively decrease, whereas the polymeric ones considerably strengthen (Fig. 2e and f). In addition, the apparent peak broadening phenomenon also reflects the tendency to form high-molecular-weight polymeric aggregates at high monomer concentration.

Two-dimensional diffusion-ordered NMR spectroscopy (DOSY) is a convenient technique to probe the size of the dynamic aggregations. As the concentration of **1** increased from 5.00 mM to 70.0 mM, the measured diffusion coefficients for the mixture of **1**–3 decreased remarkably from 3.75×10^{-10} to 5.12×10^{-12} m² s⁻¹ (Fig. 3 and Fig. S41a and b, ESI†). Based on the Stokes–Einstein equation,^{6c} the hydrodynamic radii for the resulting hyperbranched polymers **5** were determined to be 1.15 and 84.5 nm, respectively. The significant size variation behavior is highly consistent with the above concentration-dependent ¹H NMR results. Additionally, when homotritopic monomer **3** was replaced by the corresponding homoditopic secondary ammonium salt **8** (Fig. 3), representing the formation of linear supramolecular assemblies for the mixtures of **1**, **2** and **8**, the measured diffusion coefficients changed from



Fig. 2 Partial ¹H NMR spectra (300 MHz, $CDCl_3/CD_3CN$ (2 : 1, v/v), room temperature) of the supramolecular hyperbranched polymers **5** at different concentrations of **1**: (a) 2.6; (b) 4.0; (c) 5.3; (d) 8.0; (e) 16.0; and (f) 26.2 mM. Here "p" and "o" denote supramolecular polymeric and oligomeric species, respectively.



Fig. 3 DOSY spectra (400 MHz, CDCl₃, 298 K) of the supramolecular polymers (linear or hyperbranched architectures) at different concentrations of **1**: blue, 5 mM and red, 70 mM.

 5.83×10^{-10} to 8.49×10^{-11} m² s⁻¹ under the same conditions (Fig. 3 and Fig. S41c and d, ESI†). Such results illustrate that the self-assembling architectures (hyperbranched νs . linear) exert a significant impact on the size of the resulting supramolecular assemblies.

The stimuli-responsive properties of the resulting hyperbranched polymers 5 were further exploited, *via* the manipulation of the dynamic B21C7–ammonium salts recognition motif. As we know, the metal ion K⁺ exhibits a higher affinity toward B21C7 than the ammonium salt unit.^{5e} After the addition of KPF₆ (1 equiv.), the intensities of the complexed H₂₃₋₂₅ signals noticeably decreased in the ¹H NMR spectra (Fig. S42, ESI†), suggesting that K⁺ competitively complexes with B21C7 to destroy 5. Subsequent addition of 2 equiv. of 18-crown-6ether, which exhibits a higher affinity toward K⁺ than B21C7, recovered the disrupted supramolecular hyperbranched polymers, as visualized by the reappearance of the original ¹H NMR signals (Fig. S42, ESI†).

In summary, we have demonstrated that, for the bisalkynylplatinum(II) terpyridine tweezer–alkynylgold(III) diphenylpyridine recognition motif, although the binding strength is influenced by the microenvironment changes, it still maintains a highly specific complexation capability in the presence of a B21C7-based host–guest system. With the implementation of these two non-covalent recognition motifs, A_2B_3 -type dynamic supramolecular hyperbranched polymers were successfully constructed. Therefore, the current work expands the scope of the "tweezering directed self-assembly" strategy, aiding the further manipulation and application of such hierarchical supramolecular assemblies.

This work was supported by the National Natural Science Foundation of China (21274139, 91227119), and the Fundamental Research Funds for the Central Universities (WK2060200012, WK2060200012).

Notes and references

- (a) C. R. McNeill and N. C. Greenham, Adv. Mater., 2012, 21, 3840;
 (b) C. Duan, F. Huang and Y. Cao, J. Mater. Chem., 2012, 22, 10416;
 (c) X. Guo, M. Baumgarten and K. Muellen, Prog. Polym. Sci., 2013, 38, 1832;
 (d) G.-X. Jiang, C.-L. Bian, J.-Q. Ding and L.-X. Wang, Chin. J. Polym. Sci., 2013, 31, 787.
- 2 (a) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491; (b) P. M. Beaujuge and J. M. J. Frechet,

J. Am. Chem. Soc., 2011, 133, 20009; (c) A. Das and S. Ghosh, Angew. Chem., Int. Ed., 2014, 53, 2038.

- 3 Y.-K. Tian, Y.-G. Shi, Z.-S. Yang and F. Wang, Angew. Chem., Int. Ed., 2014, 53, 6090.
- 4 (a) Y. Tanaka, K. M.-C. Wong and V. W.-W. Yam, Chem. Sci., 2012,
 3, 1185; (b) Y. Tanaka, K. M.-C. Wong and V. W.-W. Yam, Chem. Eur.
 J., 2013, 19, 390; (c) Y. Tanaka, K. M.-C. Wong and V. W.-W. Yam,
 Angew. Chem., Int. Ed., 2013, 52, 14117.
- 5 (a) C. J. Zhang, S. J. Li, J. Q. Zhang, K. L. Zhu, N. Li and F. Huang, Org. Lett., 2007, 9, 5553; (b) W. Jiang, H. D. F. Winkler and C. A. Schalley, J. Am. Chem. Soc., 2008, 130, 13852; (c) X. Yan, D. Xu, X. Chi, J. Chen, S. Dong, X. Ding, Y. Yu and F. Huang, Adv. Mater., 2012, 24, 362; (d) B. Zheng, F. Wang, S. Dong and F. Huang, Chem. Soc. Rev., 2012, 41, 1621; (e) Y.-K. Tian and F. Wang, Macromol. Rapid Commun., 2014, 35, 337.
- 6 (a) V. H. S. Tellini, A. Jover, J. C. Garcia, L. Galantini, F. Meijide and J. V. Tato, J. Am. Chem. Soc., 2006, 128, 5729; (b) X. Y. Wang, H. M. Deng, J. Li, K. Zheng, X. S. Jia and C. J. Li, Macromol. Rapid Commun., 2013, 34, 1856; (c) R. C. Fang, Y. L. Liu, Z. Q. Wang and X. Zhang, Polym. Chem., 2013, 4, 900; (d) M. Hetzer, B. V. K. J. Schmidt, C. Barner-Kowollik and H. Ritter, Polym. Chem., 2014, 5, 2142.
- 7 (a) X. Yan, F. Wang, B. Zheng and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 6042; (b) K. Liu, Y. Kang, Z. Wang and X. Zhang, *Adv. Mater.*, 2013, **25**, 5530.
- 8 (a) N. Yamaguchi and H. W. Gibson, *Chem. Commun.*, 1999, 789; (b) T. Park and S. C. Zimmerman, *J. Am. Chem. Soc.*, 2006, **128**, 14236.
- 9 (a) C.-H. Wong, H.-F. Chow, S.-K. Hui and K.-H. Sze, *Org. Lett.*, 2006,
 8, 1811; (b) T. F. A. de Greef, M. M. L. Nieuwenhuizen, R. P. Sijbesma and E. W. Meijer, *J. Org. Chem.*, 2010, 75, 598.