Synthesis of novel supramolecular triads bearing a H-bonded perylene bisimide core

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ABSTRACT

Two novel hydrogen-bonded (H-bonded) triads consisting of triazine derivatives complexed with a perylene bisimide core were synthesized and characterized. NMR, UV/vis, and fluorescence spectra of these supramolecular triads confirmed the formation of strong multiple H-bonding, which were also proven to be nano-sized H-aggregates by X-ray diffraction (XRD) measurements.

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1. Introduction

During the past few decades, nanostructural aggregates of organic molecules have become significant topics due to their promising applications in light-emitting diodes, photovoltaic cells, sensors, lasers, field emitters, and field-effect transistors.[1–4] Nowadays intensive efforts to develop methods for producing organic aggregation materials with low-dimensional structures, such as nanowires, nanotubes, and nanorods, are of great importance in the development of optoelectronic and nanoelectronic devices. These novel aggregation structures and materials have been driven by their unique electronic properties, as well as by the processing advantages of organic materials relative to inorganic materials. Supramolecular concept has attracted increasing attention in macromolecular science, as one can design new supramolecular architectures with interesting morphologies derived from non-covalent interactions like hydrogen bonding, Van der Waals forces, π–π stackings, and dipole–dipole interactions.[5] Among these interactions, hydrogen bonds with higher binding energies were created as one of the most important forces to be used for the design of various molecular aggregates.[6,7] Since hydrogen bonding is moderately strong, selective, more specific, and highly directional in both solutions and surfaces, they are widely used in the construction of three-dimensional supramolecular architectures in both chemical and biological systems.[8,9]

2. Design and synthetic strategy

Supramolecular control over dye arrangement is important for improving the performance of existing optoelectronic devices and for creating new dye-based materials. Perylene bisimides (PBI) have been widely applied as red dyes for industrial purposes owing to their favorable chemical, light, and thermal stabilities.[10–12] Self-assembly, photophysical, and photochemical properties of perylene bisimides forming complementary triple H-bonded interactions were extensively studied.[13,14]

Recently, aggregates made from perylene bisimides (PBI) have attracted increasing interests, since these dyes exhibit high quantum yields, good photostability, and versatile building blocks for functional supramolecular structures.[15] Several reports revealed that perylene bisimides formed H and J type aggregates with various triazine based donors.[16–18] Nowadays, aryl amines have been commonly used in optoelectronic materials because of their good electron donating and transporting capabilities.[19–23] To the best of our knowledge, there are no reports on the studies of supramolecular nano aggregations between perylene bisimides and aryl amines. Herein, as shown in Fig. 1, we report for the first time, the construction of nano-sized H-aggregates mediated by supramolecular interactions of two novelly synthesized dodecyl trialkoxy diaryl and triaryl amine triazine donors (compounds 12 and 16) H-bonded with a perylene bisimide acceptor (PBI).

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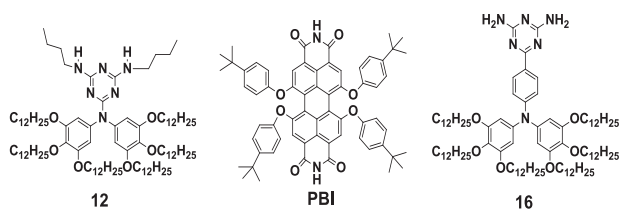
Fig. 1. Structures of 12, PBI, and 16.

5-Bromo-1,2,3-tris(dodecyloxy)benzene (4) (Scheme S1, Supplementary data) and PBI were prepared according to the literature.[24,25] As shown in Scheme S2 (Supplementary data), nitration of compound 5 with nitric acid and acetic acid gave compound 6.[26] Demethylation of compound 6 using pyridine hydrochloride at 200 °C for 3 h afforded compound 7.[27] Alkylation of compound 7 gave compound 8,[24] and reduction of compound 8 using Pd–C and hydrazine hydrate led to the corresponding amine (9).[28] Synthesis of bis[1,2,3-tris(dodecyloxy)phenyl]amine (10) was achieved by the application of Buchwald–Hartwig coupling reaction,[29] which involves the amination of compounds 4 and 9 in the presence of $Pd(OAc)_2$, P(t-Bu)$_3$, and Cs_2CO_3. In order to synthesize donor 12 (see Scheme 1), compound 10 was treated with cyanuric chloride in the presence of DIPEA followed by the nucleophilic substitution of chloride on the triazine ring by n-butylamine.[30] Compound 10 was coupled with 4-bromobenzonitrile and further refluxed with dicyandiamide using 2-methoxyethanol as solvent to obtain donor 16.[12]
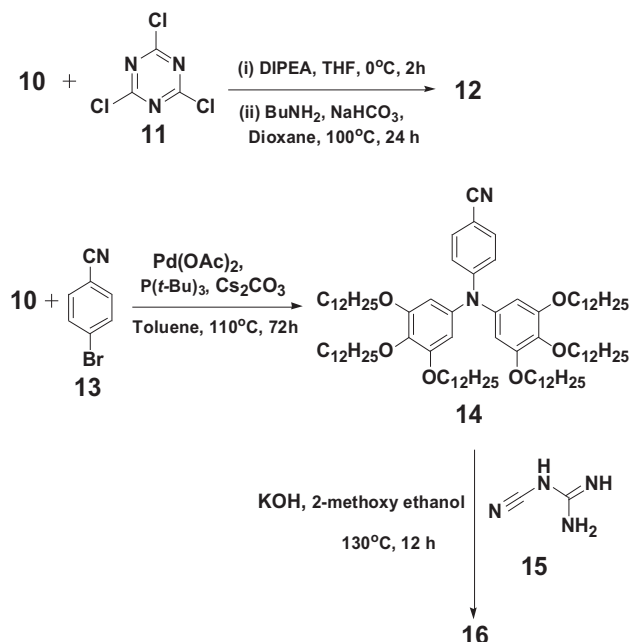
Scheme 1. Synthesis of donors 12 and 16.

3. Results and discussion

In order to verify the H-bonded interactions among moieties of supramolecular complexes, FTIR experiments were proceeded. The FT-ATR-IR spectra of compounds 12, 16, and PBI in CH_2Cl_2 (see Fig. 2) showed the free NH stretching band at 3434, 3405, and 3172 cm^{-1}, respectively. The NH stretching bands of complexes 12–PBI–12 and 16–PBI–16 (2:1 stoichiometry) in CH_2Cl_2 were observed at 3320 and 3328 cm^{-1}, respectively, which confirmed the

formation of hydrogen bonding between the donors (12 and 16) and acceptor (PBI). These results indicated that the multiple H-bonds were formed between the donors and central acceptor (PBI).[25]

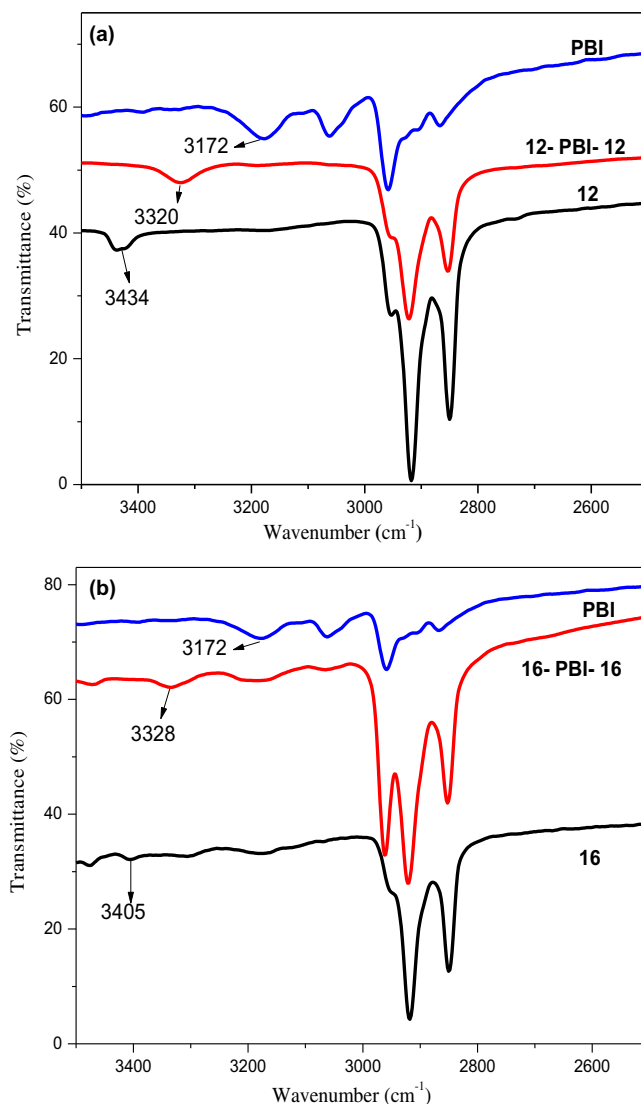Fig. 2. FT-ATR-IR spectra of (a) compounds 12 and PBI, and complex 12–PBI–12 (2:1); (b) compounds 16 and PBI, and complex 16–PBI–16 (2:1) in CH_2Cl_2 solutions.

The formation of H-bonds in supramolecular complexes 12–PBI–12 and 16–PBI–16 and the interactions of PBI with 12 and 16 were also investigated by ^{1}H NMR spectroscopic titrations in CDCl$_3$ (Fig. 3).[32–35] The concentration of PBI was kept constant (1×10^{-5} M) throughout the experiment and the changes in chemical shifts were observed as a function of increasing concentrations for compounds 12 and 16.[12] As shown in Fig. 3, the peak at δ=8.44 ppm was assigned to the N–H protons of acceptor PBI. When acceptor PBI was complexed with various equivalents of donor 12, the chemical shifts of the amidic proton in PBI changed from 8.44 to 8.72–9.20 ppm (see Fig. 3a). The consecutive shifts to lower magnetic fields were due to the decreased electron densities of the protons involved in hydrogen bonding. Similarly, the chemical shifts of N–H protons in PBI changed from 8.44 to 8.70–9.16 ppm as PBI was complexed with various equivalents of
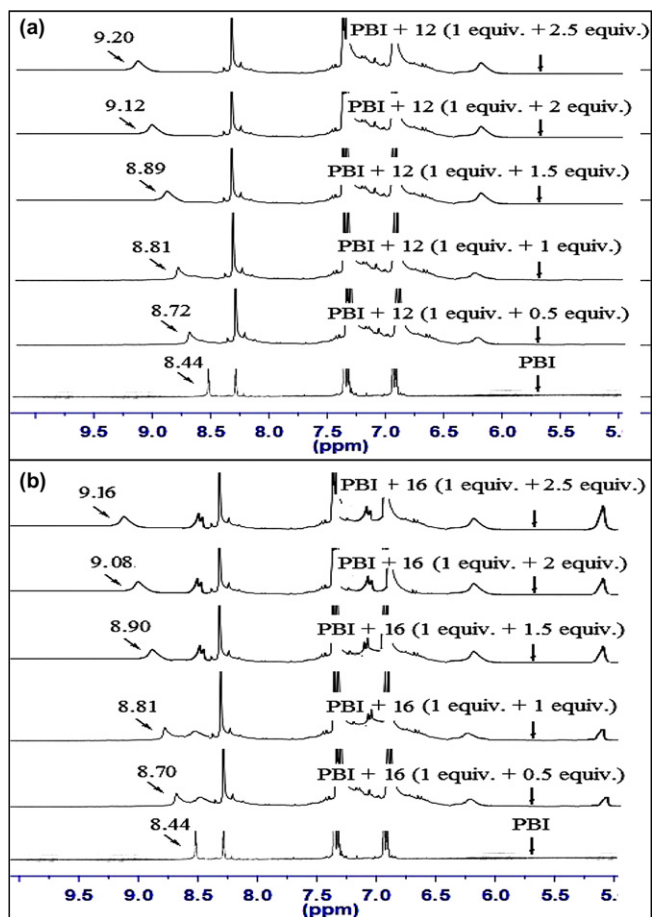
Fig. 3. ^{1}H NMR spectra of **PBI** (10 mM) titrated with compounds (a) **12** and (b) **16** (0–25 mM) in CDCl₃ at room temperature.

Fig. 4. ^{1}H NMR shifts of N–H protons in **PBI** for supramolecular triads formed by **12** and **16**, where the concentration of **PBI** was fixed at 10 mM.

Fig. 5. UV/vis titration spectra of complexes (a) **12**–**PBI**–**12** and (b) **16**–**PBI**–**16**. The concentration of **PBI** in methyl cyclohexane was kept constant at 1×10^{-5} mol/L upon the addition of **12** and **16** with different concentrations (0–2.4 equiv, with an equal span of 0.2 equiv).

16 (see Fig. 3b). During these titrations, some up-field shifts in triazine NH protons of **12** and **16** were found, but the triazine NH protons were not distinguishable because of the overcrowding in their alkyl chain regions.[36]

The downfield shifts of the amidic protons in **PBI** were due to the formation of supramolecular triads **12**–**PBI**–**12** and **16**–**PBI**–**16**, which were characteristics of the multiple H-bonded complexes.[1] As shown in Fig. 4, the analysis of the amidic protons in acceptor **PBI** as a function of increasing concentrations for compounds **12** and **16** supported the supramolecular (1:2) binding model for the H-bonded complexes.

Figs. 5 and 6 show the UV/vis and PL spectra of H-bonded complexes **12**–**PBI**–**12** and **16**–**PBI**–**16**. Upon the aliquot addition of donor **12** to **PBI**, a hypsochromic shift with absorption from 562 nm to 557 nm and emission from 591 nm to 586 nm were observed. Similarly, accompanied by blue shift H-bonded complex **16**–**PBI**–**16** showed significant decreases of absorbtion from 562 nm to 556 nm and emission from 591 nm to 585 nm. The long alkoxy chains substituted at the donor moiety played a vital role in decreasing the absorption and emission of both complexes **12**–**PBI**–**12** and **16**–**PBI**–**16**. The titration analysis of both supramolecular triads (**12**–**PBI**–**12** and **16**–**PBI**–**16**) showed the formation of 2:1 H-bonded triads. Results of UV/vis and PL titrations also revealed that both H-bonded triads **12**–**PBI**–**12** and **16**–**PBI**–**16** further stacked into H-aggregates.[31] H-aggregates exhibited broad absorption bands, which were blue shifted with respect to the donor absorption.[15] The fluorescence of H-aggregates was weak or lacking due to the fact that the optically accessible exciton states were in the upper region of the exciton band and
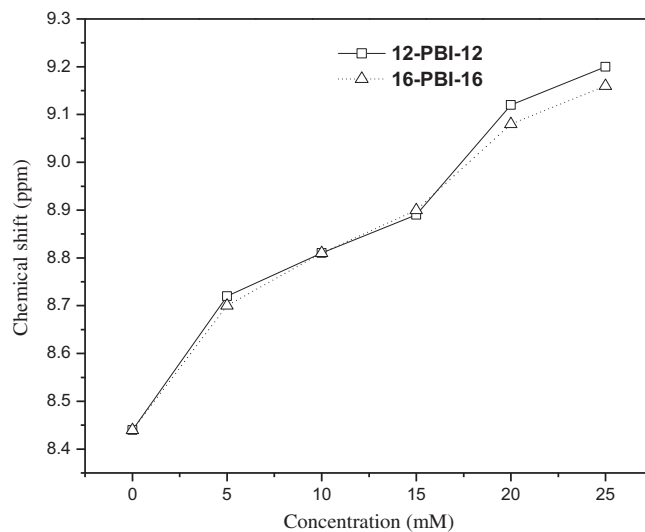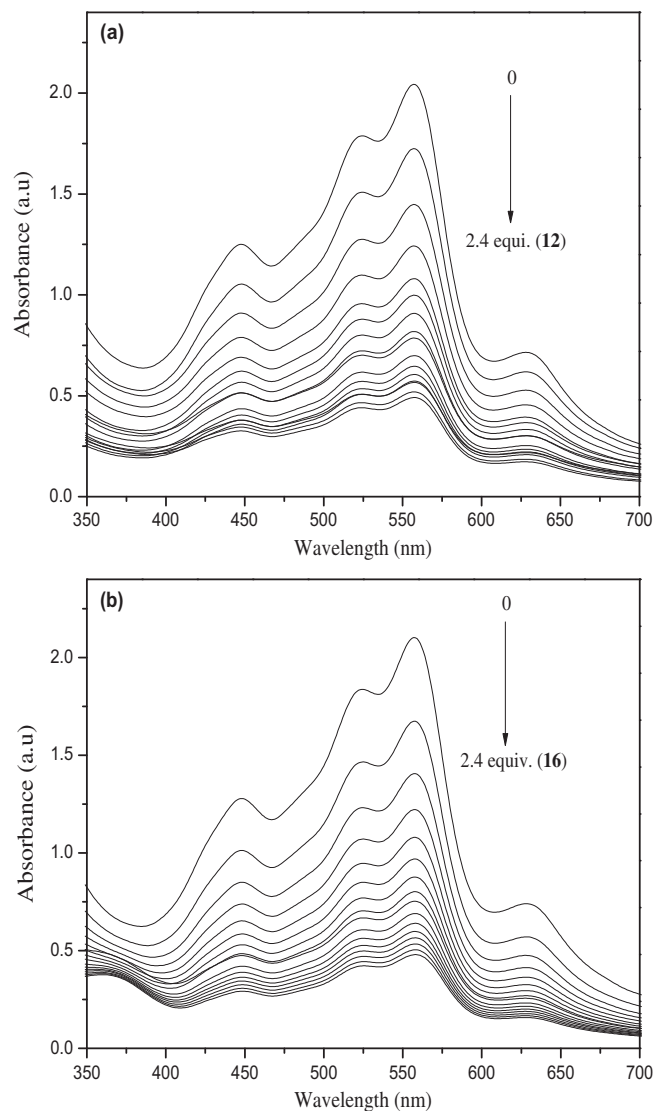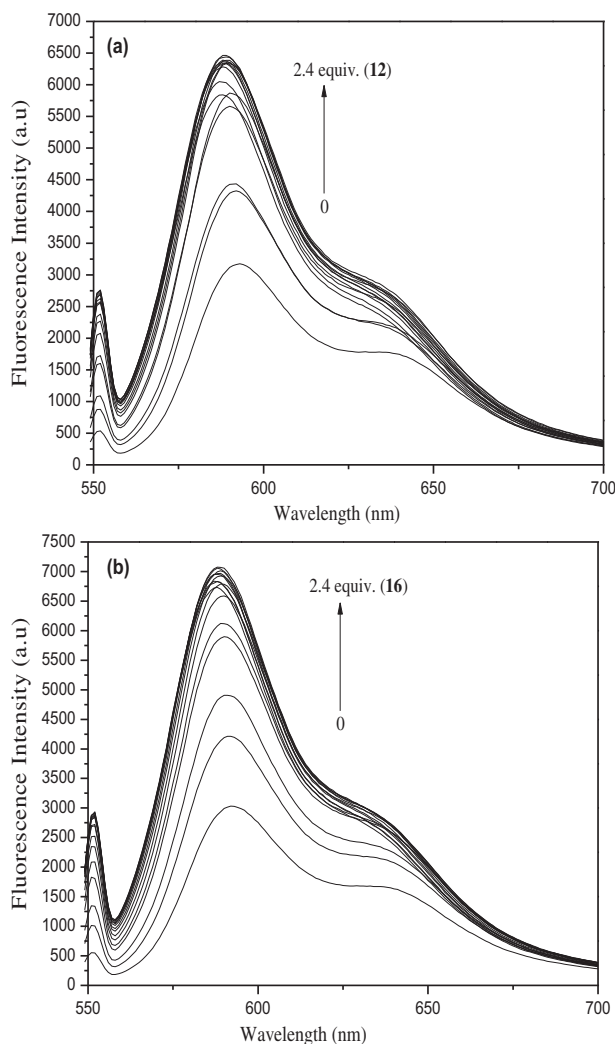
Fig. 6. PL titration spectra of complexes (a) **12**−**PBI**−**12** and (b) **16**−**PBI**−**16**. The concentration of **PBI** in methyl cyclohexane was kept constant at 1×10^{-5} mol/L upon the addition of **12** and **16** at different concentrations (0−2.4 equiv, with an equal span of 0.2 equiv). Excitation wavelength=591 nm.

Fig. 7. Job's plots for determining the stoichiometry of (a) **12**−**PBI**−**12** and (b) **16**−**PBI**−**16** based on normalized absorbance intensity at 562 nm as a function of equivalents.

their population was quickly transferred to low-lying exciton states, possessing no transition dipole to the ground state.[37] As shown in Fig. 7a and b, equivalent values of 2.07 and 1.99 were obtained by two plots of normalized absorbance intensities at 562 nm as a function of equivalents for compounds **12** and **16**, respectively, indicating a 1:2 (**PBI**−**12/16**) stoichiometric complex formation. The binding constants were calculated from standard deviation and linear fit of Fig. S1.

Fig. 8 shows the X-ray diffraction (XRD) patterns for compounds **12**, **16**, and **PBI**, along with H-bonded triads **12**−**PBI**−**12** and **16**−**PBI**−**16**, on glass substrate at room temperature. The donors (**12** and **16**) and acceptor (**PBI**) possessed strong Bragg's diffraction but after the complexation of aryl amines **12** and **16** with **PBI**, decrease in XRD intensities was observed with broad peaks. The XRD peaks are 11.6°, 20.4° for **12**−**PBI**−**12** and 13.0°, 23.1° for **16**−**PBI**−**16**. The calculated values of lattice spacings for H-bonded complexes are illustrated in Table 1. The particle size of complexes **12**−**PBI**−**12** and **16**−**PBI**−**16** were calculated using Scherrer formula.[36,38] Particle size $(D)=(0.9\lambda)/(\beta \cos \theta)$, where λ, β, and θ represent the X-ray wavelength (1.5406 Å), full width at half maximum (FWHM) of diffraction peaks, and Bragg diffraction angle at room temperature, respectively. The FWHM values of **12**−**PBI**−**12** and
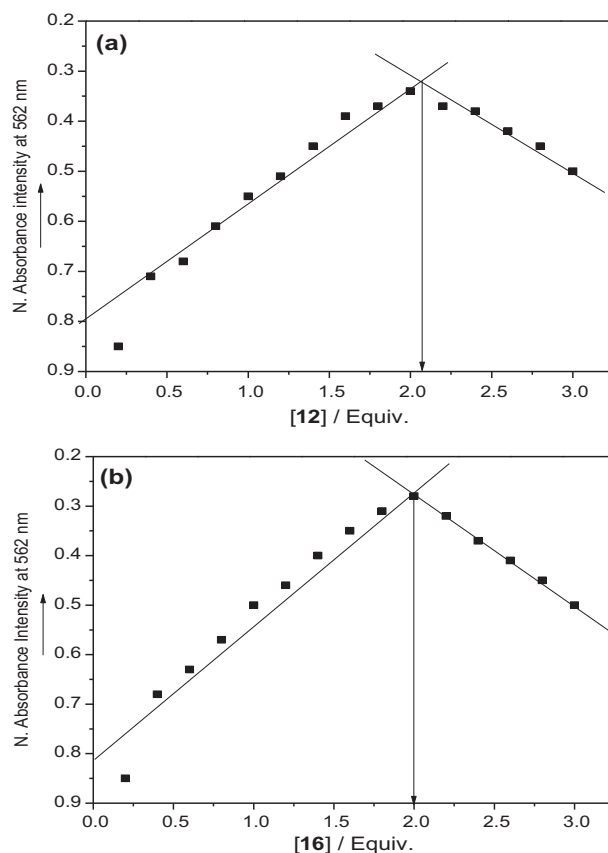
16−**PBI**−**16** are also given in Table 1. The average particle sizes of H-bonded complexes **12**−**PBI**−**12** and **16**−**PBI**−**16** are ca. 9.5 Å. Based on the aggregation size ($\sim$1 nm) of **12**−**PBI**−**12** or **16**−**PBI**−**16** acquired by XRD data along with the rough layer thickness of 3.5 Å in a planar perylene structure,[39] we can estimate that the number of ca. three-layer molecules were packed in the aggregates of **12**−**PBI**−**12** or **16**−**PBI**−**16** due to the strong π−π stacking of a planar structure in **PBI**.

4. Conclusion

In conclusion, novel H-bonded supramolecular triads of dodecyl trialkoxy diaryl and triaryl amine triazine derivatives with perylene bisimides were successfully synthesized and characterized. NMR, IR, UV/vis, and PL spectra confirmed the existence of strong multiple H-bonded interactions between the donors (**12** and **16**) and acceptor (**PBI**). Interestingly, X-ray diffraction measurements proved the formation of nano-sized particles by H-aggregates in both H-bonded triads **12**−**PBI**−**12** and **16**−**PBI**−**16**, which could be of importance for future applications. Well-defined nano-sized H-aggregates might be valuable for the development of novel functional materials utilized in nano-technological devices.

5. Experimental section

5.1. General information

All anhydrous reactions were carried out avoiding moisture by standard procedures under nitrogen atmosphere. The solvents were dried by distillation over appropriate drying agents. Reactions
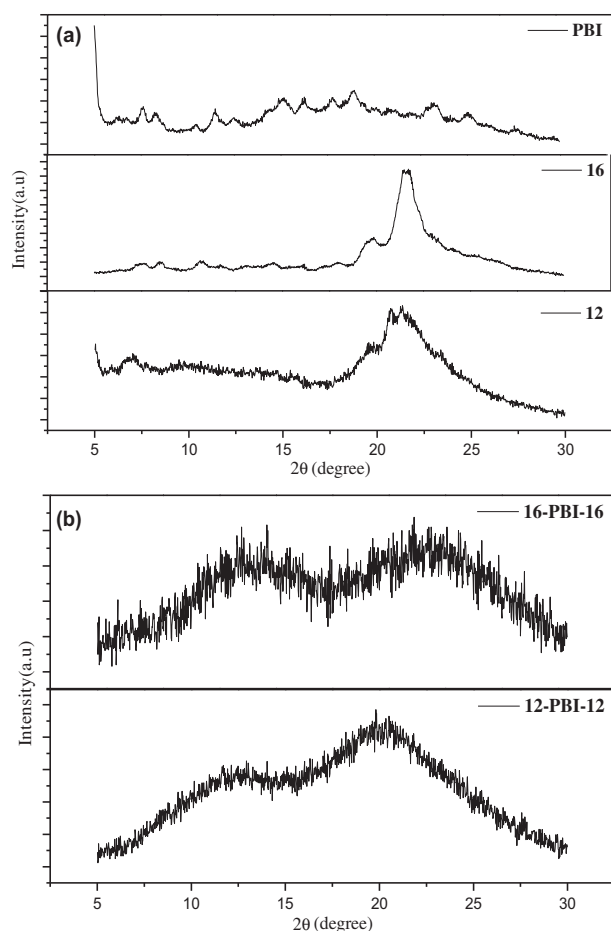
Fig. 8. XRD patterns of (a) compounds **12**, **16**, and **PBI**, (b) complexes **12**–**PBI**–**12** and **16**–**PBI**–**16**, on glass substrates at room temperature.

Table 1
FMHM values, lattice *d*-spacings, and particle sizes of H-bonded complexes **12**–**PBI**–**12** and **16**–**PBI**-16

H-bonded complex	**12**–**PBI**–**12**		**16**–**PBI**–**16**	
	θ_1	θ_2	θ_1	θ_2
2θ (°)	11.6	20.4	13.0	23.1
FWHM (°)	8.1	9.1	7.2	10.3
d-spacing (Å)	7.6	4.4	6.8	3.9
Particle size (Å)	9.9	8.9	11.1	7.9

were monitored by TLC inspection on silica gel plates. Column chromatography was generally performed on silica gel. ^{1}H and ^{13}C NMR were recorded on a 300 MHz spectrometer. The chemical shifts (δ) are reported in parts per million and coupling constants (*J*) in hertz and relative to TMS (δ 0.00) for ^{1}H NMR (s, d, t, q, m, and br denote single, double, ternary, quadruple, multiple, and broad, respectively) and chloroform-*d* (δ 7.26) and (δ 77.0) were used as reference for ^{1}H and ^{13}C NMR, respectively. Mass spectra were obtained on HR-ESI and FAB mass spectrometer. Elemental analysis was carried out by Elemental Vario EL. FT-ATR spectra were measured by using Perkin Elmer spectrum 100 series spectrometer. Spectra were collected at a resolution of 4 cm^{-1} using a deuterated triglycine sulfate detector by averaging four scans. Absorption and fluorescence spectra were measured on V-670 spectrophotometer and F-4500 fluorescence spectrophotometer, respectively. X-ray diffraction (XRD) studies of compounds on glass substrates were performed using monochromatic CuKα 1 radiation. Compounds **12**,

16, and **PBI** were dissolved in methyl cyclohexane at a concentration of 1×10^{-5} mol/L.

5.2. Bis(3,4,5,-tridodecylphenyl)amine (10)

In dry and degassed toluene (30 mL), Pd(OAc)$_2$ (130 mg, 0.6 mmol) and P(*t*-Bu)$_3$ (2.4 mL, 1.2 mmol, 10% in hexane) were introduced. After 15 min stirring, compound **4** (5.2 g, 7.4 mmol), compound **9** (4 g, 6 mmol), and Cs$_2$CO$_3$ (5.6 g, 12.5 mmol) were added. The solution was refluxed for 4 days, cooled to room temperature, and diluted with CH$_2$Cl$_2$ (100 mL). Crude mixture was filtered through Celite, evaporated to dryness, and purified on silica gel column (25% CH$_2$Cl$_2$/hexanes) to obtain **10** (4.7 g, 60%) as light yellow solids. Mp 47–50 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.87 (t, 18H, *J*=6.6 Hz, Me), 1.27 (br, 96H, CH$_2$) 1.40–1.47 (m, 12H, CH$_2$), 1.69–1.82 (m, 12H, CH$_2$), 3.87–3.91 (m, 12H, CH$_2$), 5.39 (s, 1H, NH), 6.25 (s, 4H, ArH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 69.03, 73.56, 97.23, 132.67, 139.30, 153.64.

5.3. N^2,N^4-Dibutyl-N^6,N^6-bis(3,4,5-tris(dodecyloxy)phenyl)-1,3,5-triazine-2,4,6-triamine (12)

N,N-Diisopropylethylamine (DIPEA) of 0.32 mL (1.87 mmol) was added to a solution of 0.3 g (1.17 mmol) 2,4,6-trichloro-1,3,5-triazine **11** in anhydrous tetrahydrofuran (THF) (30 mL). The reaction mixture was cooled to 0 °C, and a solution of **10** (1.5 g, 1.17 mmol) in THF (20 mL) was added dropwise over 1 h at this temperature. After completion of the addition, the reaction mixture was warmed to room temperature, and stirred for an additional 12 h until the starting material disappeared. The resulting white precipitate was filtered off and the filtrate was evaporated under reduced pressure. The obtained crude compound (1.5 g, 90%) was dissolved in dioxane (60 mL) mixed with *n*-butylamine (0.5 mL, 5 mmol) and NaHCO$_3$ (0.5 g, 6 mmol), and then the solution was refluxed for 12 h. The reaction mixture was poured into 200 mL of water and extracted three times with CH$_2$Cl$_2$. The combined organic extract was washed with water, brine, dried over anhydrous MgSO$_4$, and evaporated to dryness and purified on silica gel column (20%EtOAc/hexanes) to afford **12** (1.4 g, 85%) as a low melting solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.87 (t, 24H, *J*=7.5 Hz, Me), 1.26 (br, 96H, CH$_2$) 1.41 (br, 16H, CH$_2$), 1.69–1.81 (m, 12H, CH$_2$), 3.17 (br, 4H, NHCH$_2$), 3.82–3.95 (m, 12H, OMe), 4.80 (br, 2H, NH), 6.44 (s, 4H, ArH); ^{13}C NMR (75 MHz, CDCl$_3$): δ 14.10, 20.02, 22.68, 26.16, 29.36, 31.92, 40.35, 69.03, 73.38, 106.81, 135.79, 139.40, 152.60, 166.24, and 179.61. HRMS-ESI: (M$^+$) found 1496.3556. C$_{95}$H$_{174}$N$_6$O$_6$ requires 1496.3573. Anal. found: C, 75.12; H, 11.74; N, 5.59. C$_{95}$H$_{174}$N$_6$O$_6$ requires : C; 76.25; H, 11.72; N, 5.72.

5.4. 4-(Bis(3,4,5-tris(dodecyloxy)phenyl)amino)benzonitrile (14)

In dry and degassed toluene (20 mL), Pd(OAc)$_2$ (34 mg, 0.156 mmol) and P(*t*-Bu)$_3$ (0.6 mL, 0.3 mmol, 10% in hexane) were introduced. After 15 min stirring, 4-bromobenzonitrile **13** (0.28 g, 7.0 mmol), compound **10** (2 g, 1.56 mmol), and Cs$_2$CO$_3$ (2.2 g, 6 mmol) were added. The solution was refluxed for 3 days, cooled to room temperature, and diluted with CH$_2$Cl$_2$ (100 mL). The crude mixture was filtered through Celite, evaporated to dryness, and purified on silica gel column (20%CH$_2$Cl$_2$/hexanes) to afford light yellow solid **14** (1.6 g, 72%). Mp 56–59 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.87 (t, 18H, *J*=6.9 Hz, Me), 1.25 (br, 96H, CH$_2$) 1.38–1.48 (m, 12H, CH$_2$), 1.69–1.77 (m, 12H, CH$_2$), 3.77–3.96 (m, 12H, OMe), 6.29 (s, 4H, ArH), 6.97 (d, 2H, *J*=9 Hz, ArH), 7.62 (d, 2H, *J*=9 Hz, ArH). ^{13}C NMR (75 MHz, CDCl$_3$) δ 69.55, 73.89, 101.88, 105.46, 119.26, 120.28, 133.39, 136.38, 141.25, 152.03, 154.14.

5.5. 6-(4-(Bis(3,4,5-tris(dodecyloxy)phenyl)amino)phenyl)-1,3,5-triazine-2,4-diamine (16)

In a round-bottom flask, compound **14** (1.5 g, 1 mmol) and dicyandiamide **15** (0.1 g, 1.3 mmol) were dissolved in 2-methoxyethanol (30 mL). After adding KOH (0.34 g, 6 mmol), the solution was stirred at 100 °C for 24 h. After cooling the reaction mixture to room temperature, 100 mL of brine was added and the aqueous phase was extracted three times with dichloromethane (100 mL). The organic fractions were collected and dried over MgSO$_4$. After evaporation of the solvent, the product was purified with silica gel column chromatography (30% EtOAc/hexanes) to afford **16** (0.6 g, 38%) light yellow powders. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.87 (t, 18H, J=7.5 Hz, Me), 1.25 (br, 96H, CH$_2$) 1.37–1.48 (m, 12H, CH$_2$), 1.69–1.77 (m, 12H, CH$_2$), 3.76–3.97 (m, 12H), 5.19 (s, 4H, NH$_2$). 6.03 (s, 4H, ArH), 7.03 (d, 2H, J=8.7 Hz, ArH), 8.12 (d, 2H, J=8.7 Hz, ArH). ^{13}C NMR (75 MHz, CDCl$_3$) δ 69.28, 73.70, 104.70, 124.59, 128.30, 129.51, 135.20, 142.38, 141.40, 153.71, 169.63, 172.15. HRMS-FAB: (M$^+$), found 1459.2565. C$_{93}$H$_{162}$N$_6$O$_6$ requires 1459.26. Anal. found: C, 76.12; H, 11.16; N, 5.82. C$_{93}$H$_{162}$N$_6$O$_6$ requires: C; 76.49; H, 11.18; N, 5.75.

Acknowledgements

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.07.015.

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