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Synthesis and optical properties of perylene diimide derivatives with triphenylene-based dendrons linked at the bay positions through a conjugated ethynyl linkage

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ABSTRACT

A number of groups including trimethylsilyl, phenyl, triphenylene, and triphenylene-based dendron have been linked to the bay positions of a perylene diimide (PDI) core through an ethynyl bridge. The photophysical properties of the resulting bay-substituted PDI derivatives have been carefully studied in different solvents and as thin films. Without any capping group, the two ethynyl bay-substituted PDI derivates **PAT** and **PRT** both aggregate strongly even in dilute solutions but in different perylene-perylene $\pi-\pi$ stacking modes; **PRT** aggregates through slipped (or longitudinal) stacking while **PAT** selfassembles by rotational (or cross) stacking. With capping groups, the perylene core stacking is completely blocked for **PATS** in both solution and solid film. For **PRTS**, the slipped stacking is observed only for its film sample, while for PTB, association only occurs after excitation (excimer formation). When triphenylene or triphenylene-based G1 dendron is attached to the acetylene bridge, the resulting donor-acceptor systems (PTG0 and PTG1) exhibit strong electronic coupling between the dendritic donors and the PDI acceptor, leading to significantly red-shifted absorption bands. The conjugated linkage also facilitates photoinduced electron transfer from the triphenylene or triphenylene dendron to the PDI core, effectively quenching fluorescence emissions of both the donor and the acceptor. The significantly redshifted absorption bands and the efficient photoinduced electron transfer observed on PTG0 and PTG1 indicate that these new PDI derivatives may find applications in solar cells.

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1. Introduction

Perylene diimide (PDI) derivatives are one of the most extensively studied n-type organic semiconductors, not only due to their strong electron accepting^{1–3} and fast electron transporting properties,^{4,5} but also due to their remarkable chemical and thermal stability.^{6–8} An attractive feature of the PDI core is that structural modifications at either its bay positions and/or the imide positions can be readily accomplished, enabling the optimization of its properties.⁹ One property often targeted for improvement is its absorption wavelength range. For applications in certain molecular electronic devices such as sensors,^{10–13} photovoltaic cells,^{12,14–18} it is often desirable to extend its absorption to longer wavelength regions. For this purpose, substitution at the bay positions is favored since substituents at the imide positions have negligible ground state electronic interaction with the PDI core due to the

existence of a node plane at the imido position.¹⁸ Substituents at the bay positions,^{19–25} particularly those with π -conjugated linkages,^{26–30} however could effectively modulate electronic states of the PDI core.

Among various conjugated linkages, the acetylene bridge is found to be quite effective in modulating the PDI core's bandgap, as the carbon–carbon triple bond linkage imposes low steric hindrance when tethered to the bay positions and thus is favorable for creating extended conjugated scaffold.³¹ The extension of π -conjugation from the PDI core through the acetylene bridge to attached electron donors, such as porphyrin,³² phthalocyanine,³³ and arylamine,³⁴ leads to ultrafast photoinduced intramolecular charge separation. While a number of π -conjugated systems have been anchored to the bay positions of the PDI core through the acetylene linkage, there is still lack of systematic study in regard to the correlation between the extent of extended π -conjugation and the chromophore's bandgap. The aggregation behavior of such π -extended PDI systems in solid states is also not well understood. In this contribution, we report the synthesis of a set of PDI derivatives



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with π -conjugation progressively extended at PDI's bay positions. A systematic photophysical studies on both their solutions and solid films have been carried out. It is shown that substitution at the bay area not only affects the π -extension, but also has a profound effect on the mode of PDI core aggregation.

2. Results and discussions

2.1. Synthesis of PDI derivatives

Chart 1 list the structures of PDI derivatives subjected to this study. Compounds PRT and PRTS have a linear hexyl chain at the imido position while the rest of the compounds possess a 2,6diisopropylphenyl group at the imido position. All seven compounds have an ethynyl group at the 1, 7-bay positions of the PDI core. The PDI's π -system is extended through the acetylene bridge to benzene (PTB), triphenylene (PTGO), and a triphenylene dendron (PTG1).

The synthetic approaches to the above PDI derivatives are shown in Schemes 1 and 2. A dibrominated perylene dianhydride mixture containing 1,6- and 1,7-regioisomers was synthesized according to a literature procedure.³⁵ Without separating the two regioisomers due to their poor solubility in common organic solvents, the mixture was reacted with hexylamine in 1:1 water/1butanol solvent mixture, converting the dianhydride to a diimide. The isolation of the 1.7-isomer from the 1.6-isomer using conventional column chromatography or recrystallization techniques using common organic solvents was unsuccessful. The mixture was thus coupled with triisopropylsilyl (TIPS) acetylene to yield PRTS initially as a 1,6- and 1,7-regioisomeric mixture. At this stage, the pure 1,7-isomer was isolated from the 1,6-isomer by column chromatography. The bulky TIPS group appears to limit PDI core aggregation and makes the separation of the regioisomers easier. Previously it has been reported that the triphenylsilyl group can also be used for the straightforward separation of the 1,7-isomer from the 1,6-isomer by column chromatography.³² It should be noted that the trimethylsilyl-analog of PRTS does not allow isomeric separation using similar separation techniques. Clearly the bulkiness of ethynyl's capping groups is critical for isomer separation. The TIPS protected 1,7-diethynyl PDI (PRTS) was desilylated



⁽a) 1:1 water: 1-butanol, 70 °C, 19h, 48%

(b) Pd(PPh₃)₂Cl₂, CuI, Et₃N or iPr₃N, DMF, 90 °C, 24h; (c) TBAF, THF, r.t., 30 min

1,7- isomer

PRTS

PRT

Scheme 1. Synthesis of PRTS and PRT.



Scheme 2. Synthesis of PDI derivatives PATS, PAT, PTB, PTG0, PTG1.

with tetrabutylammonium fluoride, leading to compound **PRT** in 45% yield.

When 2,6-diisopropylphenyl, instead of the *n*-hexyl group, was introduced to the imido positions, the pure 1,7-dibromo-PDI derivative (**PBr**) can be isolated by simple recrystallization (Scheme 2).³⁶ The pure **PBr** was subjected to the Sonogashira coupling reaction with trimethylsilylacetylene to yield compound **PATS** in 65% yields, which was then converted to **PAT** by routine desilylation.

Our initial attempt toward PTG0 and PTG1 synthesis involves the reaction of PAT or PATS with triflate-functionalized triphenylene (GOOTf) and triphenylene-based dendron G1OTf (replacing the ethynyl group of G1T with a triflate gives G1OTf) since both GOTf and G1OTf had previously been synthesized during our research on triphenylene-based dendrons.³⁷ Unfortunately, Pdcatalyzed coupling reactions between PAT and GOOTf, PATS and GOOTf were both unsuccessful, presumably due to the low reactivity of the triphenylene-attached triflate group. The synthetic focus was then shifted to utilize **PBr** as the coupling reagent. For this purpose, ethynyl-functionalized triphenylene (GOT) and triphenylene-based G1 dendron (G1T) were synthesized from GOOTf and G1Tf, respectively.³⁷ Direct Sonogashira coupling between PBr and ethynylbenzene, GOT, or G1T successfully yielded PTB, PTG0, and PTG1, respectively. PTG0 and PTG1 are only partially soluble in some organic solvents, such as chloroform, THF, and DMF, even at elevated temperatures. The poor solubility of the product made the purification process challenging and led to the low yields of isolated pure products.

2.2. Structural characterizations

Among the seven PDI derivatives, **PRTS**, **PATS**, and **PTB** are soluble in common organic solvents and their ¹H NMR spectra show well-resolved sharp signals, which can all be unambiguously

assigned to their respective structures (See Figs. S1–S3 in Supplementary data). Compared to the ¹H NMR spectrum of **PBr** (Fig. S3), one observes that when the Br group of **PBr** is replaced with an acetylene bridge, proton H1 (see Fig. 1 for proton labeling) shifts downfield by more than 0.7 ppm while protons H2 and H3 shows negligible changes in their chemical shifts. The significant downfield shift of H1 is likely due to the deshielding effect of the adjacent acetylene π electrons. The capping group at the end of the acetylene bridge, whether a TMS in **PATS**, TIPS in **PRTS** or phenyl in **PTB**, appears to have minimal effect on the chemical shifts of the protons on the PDI core.

When the TIPS group of **PRTS** is removed, the solubility of the resulting compound **PRT** is significantly lowered. The ¹H NMR spectrum of **PRT** shows broad signals and is concentration dependent. As shown in Fig. 1, when the concentration increases, the aromatic proton signals are broadened and shift upfield. While three aromatic proton signals are clear and well separated, extremely broad humps in both the aromatic and aliphatic regions are discernible. Even for a highly diluted solution where the three aromatic signals are sharp and their multiplicities are clear, the broad hump covering the entire aromatic region is still noticeable. These results indicate that for **PRT** there is strong inter-perylene π - π stacking, even in highly diluted conditions.

Unlike **PRT**, the ¹H NMR spectrum of **PAT** does not show the broad humps, but rather two sets of perylene proton signals (Fig. S4), one sharp and one broad. The broad signal of H1 is shifted upfield while those of H2 and H3 are shifted downfield, when compared to their respective sharp signals. The protons on the phenyl ring, however, give only sharp, multiplicity-clear signals, i.e., no broad signals. These results indicate that the perylene core of **PAT** π stack as well, but perhaps through a rotational offset, likely due to the bulkiness of the 2,6-diisopropylphenyl rings, which prevent parallel inter-perylene π -stacking. When two perylene



Fig. 1. ¹H NMR spectra of PRTS and PRT in CDCl₃.

rings cross-stack (i.e., 90° rotational offset), the π -electrons of one perylene ring will have a shielding effect on H1 but deshielding effect on H2 and H3, resulting in upfield shift for H1 but downfield shift for H2 and H3. The lack of broad hump signals perhaps indicates that the π -stacking of **PAT** is limited to small aggregates (i.e., lower oligomers).

PTG0, albeit with two hexyloxy side chains on each triphenylene ring, shows poor solubility in all solvents tested, even at elevated temperatures. The solubility is so poor that its ¹H NMR spectrum is dominated by solvent signals (Fig. S5). While one can identify characteristic proton signals from both the perylene core and the attached triphenylene units after expanding the spectrum, the messy spectrum provides no proof of either the structure or the purity of the product. Thin-layer chromatography (TLC), however, confirms one single pure compound and MALDI-TOF analysis shows only two peaks at 1672.96 and 1694.94 (Fig. S6), which correspond to M^+ (1672.13) and $M+Na^+$ (1695.12), respectively. Elemental analysis corroborates the purity and structure of **PTG0**.

When a bulkier triphenylene-based G1 dendron is attached to the acetylene bridge, the resulting **PTG1** exhibits better solubility in common organic solvents than **PTG0**. The ¹H NMR spectrum of **PTG1** (Fig. S7) in CDCl₃ shows broad but clear signals. Although signals associated with the G1 dendron dominate the spectrum, one can still clearly identify peaks attributed to the perylene core. It is interesting to note that perylene's H1 protons in **PTG1** are further downfield shifted from 10.2 ppm observed for **PATS**, **PRTS**, and **PTB** (Fig. S3) to 10.6 ppm (Fig. S7), presumably reflecting a stronger π conjugation which likely increases the π -electron density of the perylene core due to the electron-donating nature of the G1 dendron. The structure and purity of **PTG1** is again confirmed by TLC (one single spot) and MALDI-TOF analysis, which shows one single peak in the 500–5000 range at 3702.70 (Fig. S6) corresponding to M+Ag⁺ (3702.55).

2.3. Photophysical properties

The optical properties of all seven PDI derivatives, together with **PBr**, **G0T**, and **G1T**, were studied in dilute chloroform solutions, hexane solutions, and as solid films. The results are discussed in the following sections.

2.3.1. Steady-state absorption. Perylene and perylene diimide compounds are well known organic dyes, which show intense absorption in the visible spectral range. Without exception, the seven PDI derivatives show rich absorption bands in the visible range as well. As shown in Fig. 2, when the bay substitution changes



Fig. 2. UV/vis absorption spectra of PBr, PATS, PTB, PTG0, and PTG1 in dilute chloroform solutions.

from Br to TMS-ethynyl, phenylethynyl, triphenylene-ethynyl, and G1-ethynyl, all absorption bands continuously shift to longer wavelengths. The longest wavelength absorption bands of **PBr**, **PATS**, **PTB**, **PTG0**, and **PTG1** are 528, 550, 566, 614, and 626 nm, respectively, indicating that the PDI core's π system is increasingly extended through the acetylene bridge to the attached π -units. As the π -conjugation expands, the extended π -system gradually loses some identity of the PDI core, which is reflected in their absorption spectra where fine structures are diminished.

In addition to absorption bands in the visible range, **PTG0** and **PTG1** also show even stronger absorptions in the 300–450 nm range. PDI core shows only a very weak absorption band at around 400 nm (S0–S4 transition), while **GOT** exhibits a weak flattened hump from around 320 nm–370 nm. The intense peak at 358 nm of **PTG0** is clearly a new transition not seen in the absorption spectrum of a 2:1 **GOT/PTB** physical mixture (Fig. S8). This transition is likely a π – π * transition involving a π -system extending and originating from the triphenylene ring. Due to covalent attachment to the PDI core, the normally symmetry forbidden π – π * transition of the triphenylene's π system becomes symmetry allowed after extending beyond the acetylene bridge, leading to an intense absorption band at 358 nm. For **PTG1**, the intense absorption band at 352 nm can be assigned to the absorption of the G1 dendron as **G1T** shows similar absorption bands in the 320–430 nm range (Fig. S9).

Unlike PATS and PRTS, as well as PBr and PTB, all of which show typical PDI core absorptions with resolved multiple bands, the absorption spectra of PAT and PRT in dilute chloroform solutions, as shown in Fig. 3. show one broad structureless band in the visible range and a long tail, features typical of ground state aggregates. The ratio of the absorptivity at 550 nm (the 0-0 band) to that at 500 nm (the 0–1 band) is 2.7 for both PATS and PRTS, but only 1.1 for PAT and 0.8 for PRT; the significant decrease in this value is again indicative of strong aggregation.³⁸ While both **PAT** and **PRT** appear to be prone to solution aggregation, there are noticeable differences between their absorption behaviors. First of all, the absorption ratio of I_{550}/I_{500} is lower for **PRT** so much so that the λ_{max} of **PRT** is now around 500 nm. The solution spectrum of **PRT** closely matches that of its film spectrum in the visible range, clearly indicating strong aggregation of **PRT** even in a dilute solution, which is consistent with NMR results. The film spectrum of PAT, on the other hand, is broadened to longer wavelengths by about 15 nm, indicating PAT aggregation in solutions is not as strong as that of PRT, again consistent with NMR results. As mentioned



Fig. 3. UV/vis absorption spectra of PAT (black) and PRT (red) in dilute chloroform (dark line) and as thin films (light line).

earlier, the PDI core in **PAT** likely adopts cross (rotational) $\pi - \pi$ stacking. Theoretical calculation has shown that such rotational aggregates can indeed lead to 'a single broadened peak that spans a 4000 cm⁻¹ range, devoid of structure'.³⁴

2.3.2. Steady-state fluorescence. In dilute chloroform solutions, PDI derivatives **PBr**, **PATS**, **PRTS**, and **PTB** are all highly fluorescent with unity quantum yield. **PAT**, however, has a fluorescence quantum yield of only 0.16 (λ_{ex} =512 nm) while **PRT** is non-fluorescent. The significant fluorescence quenching of **PAT** and **PRT** is consistent with their fore-stated aggregation behavior in solutions.

PTG0 and **PTG1** are also poor fluorescence emitter. Although π conjugation extends over both the PDI core and the triphenylene G0 or G1 dendron, there appears to be two types of extended π systems in both PTGO and PTG1, one roots from the PDI core, which absorbs in the visible range and the other originates from the G0 or G1 dendron which contributes to the absorption bands in the 300-450 nm range. Thus, depending on the excitation wavelength, PTG0 and PTG1 may have two different excitons, which emit light of different wavelengths, if excitonic energy and/or electron transfer is not so efficient between them. It turns out though that both PTG0 and PTG1 in chloroform show very weak fluorescence emissions no matter what the excitation wavelength is. If G0 or G1 is excited (λ_{ex} <400 nm), both **PTG0** and **PTG1** emits weakly around 440 nm (Fig. 4a) with quantum yields less than 0.01. To confirm that such emissions are not due to any possible residual unreacted GOT or G1T. the fluorescence and excitation spectra of PTG1 and PTG0 are compared with those of G1T and G0T, respectively, in Fig. 4. G1T is moderately fluorescent with an emission maximum at 427 nm and a quantum yield of 0.3. The emission wavelength of PTG1 (442 nm) is red-shifted by 15 nm compared to that of G1T. The excitation spectra of PTG1 and G1T also differ significantly. The most striking difference is that the excitation spectrum of PTG1 shows a sharp and strong peak at 416 nm where G1T does not absorb (Fig. 4b). When the fluorescence and excitation spectra of **PTGO** are compared with those of **GOT**, the differences are even more dramatic: PTGO shows 25 nm red-shifted emissions and redshifted excitation bands at 365 and 393 nm, which are missing in the excitation spectrum of GOT (Fig. 4b). These results exclude the observed weak PTGO and PTG1 emissions as those of unreacted GOT or G1T. The fact that the strongest excitation for PTG1 or PTG0 occurs at wavelengths where G1T or G0T does not even absorb indicates that the exciton responsible for the 440 nm emission is due to a π -system, which extends beyond the G1 or G0 dendron, the acetylene bridge and into at-least part of the PDI core.

If the PDI is excited, **PTG1** in chloroform emits at 648 nm while **PTG0** shows no fluorescence. In hexane, though **PTG0** does show weak PDI fluorescence with a maximum emission wavelength at 607 nm and a quantum yield of 0.03. Details on solvent effects are discussed later. Similar to their absorption spectra shown in Fig. 2, continuous red-shift in the maximum emission wavelength is also observed, as clearly shown in Fig. 5. The maximum emission wavelengths for **PBr**, **PATS**, **PTB**, **PTG0**, and **PTG1** are 545, 563, 590, 607 (in hexane), and 648 nm, respectively.

2.3.3. Solvent effect and thin film optical properties. The absorption spectra of all seven PDI derivatives have been studied in hexane and as thin films as well. Comparison of their optical properties in different solvents and as thin films provides some insight into their self-assembly behavior.

First, the absorption, fluorescence emission, and excitation spectra of **PATS** and **PRTS** are compared. As shown in Fig. 6, **PATS** and **PRTS** show nearly identical solution absorption and fluorescence emission behavior: same absorption and emission wavelengths, same extent of blue shift when the solvent is changed from chloroform to hexane. The absorption and emission spectra of their



Fig. 4. Fluorescence emission (a) and excitation (b) spectra of PTG1, G1T, PTG0, and G0T.



Fig. 5. Normalized fluorescence emission spectra of **PDI** derivatives in dilute chloroform solutions (λ_{ex} >400 nm) except for **PTG0** whose **PDI** emission was measured in hexane. The inset shows the emission spectra of **PTG0** and **PTG1** in chloroform when excited at 350 nm.

films, however, are very different. While the film of **PATS** shows identical absorption wavelengths to those of its chloroform solution; the absorption spectrum of **PRTS** film has stark difference from that of its chloroform solution (Fig. 6a). Most notably, a relatively strong absorption tail extending beyond 700 nm is observed. The 0–0 transition seen as the strongest absorption band in both chloroform and hexane solutions disappeared while the 0–1 transition becomes the strongest one in the visible region. The fluorescence emission difference between **PATS** and **PRTS** is also obvious: **PRTS** emits at much longer wavelength (λ_{em} =650 nm) than that of **PATS** (λ_{em} =600 nm). The excitation spectrum of **PATS** film is also significantly red-shifted compared to that of **PATS**

(Fig. S10). These data suggest that the perylene-perylene $\pi - \pi$ stacking in solid films is lacking or very limited for **PATS** but strong for **PRTS**. The limited aggregation of **PATS** may be resulted from the complete blocking effect of the TMS groups at the bay and the diisopropylphenyl units at the imido ends. **PRTS**, on the other hand, has only the bay positions blocked by the silyl groups while its two imido ends are relatively open due to linear alky substitutions. Thus, slipped stacking, forming J-aggregates, is possible, which may account for the much red-shifted absorptions and emissions. It is worth noting that **PATS** and **PRTS** bear different silyl groups. As mentioned earlier, the TMS analog of **PRTS** could not be obtained in pure isomeric form. Although one can synthesize the TIPS analog of **PATS**, that compound is expected to show little or no aggregation, just like **PATS** since TIPS is an even bulkier substituent.

Like PATS and PRTS, PTB is highly fluorescent in both chloroform and hexane. The optical properties of PTB also show similar solvent dependence: when the solvent is changed from chloroform to hexane, the maximum absorption wavelength λ_{max} , maximum emission wavelength λ_{em} , and maximum excitation wavelength λ_{ex} are all blue-shifted by about 14 nm. The emissions of the PTB film however are quite unique where two distinct peaks, one at 605 nm and the other at 675 nm are observed as clearly shown in Fig. 7. The excitation spectra of these two emission peaks are nearly identical and closely match that of PTB's chloroform solution (Fig. 7, center). The absorption spectra of the film and the chloroform solution also resemble each other except for around 10 nm red-shift in the absorption band edge. Taking these data together, one may conclude that the 605 nm emission is due to monomeric emission while the 675 nm emission is due to aggregate emission. The similar excitation spectra of 675 nm emission to that of 605 nm emission, coupled with the lack of new absorption peaks in the film absorption spectrum indicate that the 675 nm emission band may be of excimer nature (dynamic aggregates), which is different from PRTS where aggregation occurs at the ground state. It is possible that at ground state the acetylene-linked phenyl ring is twisted in respect to the perylene ring, which prevents perylene–perylene π – π stacking. In the excited state, one of the phenyl rings and the perylene core may be planar (due to the charge transfer nature of the



Fig. 6. UV/vis absorption (a) and fluorescence emission (b) spectra of PATS (top) and PRTS (bottom) in chloroform (black), hexane (blue) and as thin films (red).



Fig. 7. Fluorescence emission, excitation, and absorption spectra of **PTB** in chloroform (red), hexane (blue), and as thin film (red).

exciton), which is conducive to excimer formation. Clearly, substitution at the bay area not only affects the π -extension, but also has a profound effect on the mode of PDI core aggregation.

Unlike PDI derivatives discussed so far (**PBr**, **PATS**, **PRTS**, **PTB**), all of which show blue shift in absorption and fluorescence emission when the solvent is changed from chloroform to hexane, **PTGO** however shows red-shift in the absorption spectrum as shown in Fig. 8a. The absorption spectrum of **PTGO** in hexane closely matches that of **PTGO** film, particularly for the absorption band edge.



Fig. 8. UV/vis absorption (a) and fluorescence emission (b) of **PTG0** in chloroform (black), hexane (blue) and, as thin films (red). The excitation wavelength is 370 nm (except for the inset).

Apparently, **PTG0** molecules aggregate in hexane solutions. Interestingly, **PTG0** in hexane is far more fluorescent than in chloroform. As shown in Fig. 8b, when excited at 370 nm (**G0T** excitation), **PTG0** in hexane not only give structured emissions in the 360–500 nm range, but also a longer wavelength emission at 605 nm. As mentioned earlier, the short wavelength emissions are attributed to the extended π -system originating from perylene-attached **G0T** while the longer wavelength emission is assigned to the π -system extending out from the PDI core. When the PDI core is excited, the longer wavelength emission is again observed. The fluorescence quantum yields of **PTG0** in hexane are 0.01 at 370 nm excitation and 0.03 at 570 nm excitation. It is worth noting that **PTG0** in chloroform gives no PDI emissions, no matter what excitation wavelength is used and **PTG0** film is non-fluorescent.

To identity the emitting species of **PTG0** in hexane, fluorescence excitation spectra at emitting wavelengths of 440 nm and 605 nm were recorded and compared with its absorption spectrum. As shown in Fig. 9, the excitation spectrum with λ_{em} =440 nm shows well-structured peaks and a steep spectral band edge. The spectrum resembles the one in chloroform (Fig. 4b) except for ~8 nm blue



Fig. 9. Excitation spectra of **PTG0** in hexane with the emission wavelength set at 440 nm (red) or 605 nm (black), in comparison with its absorption spectrum (dotted line).

shift. When the emission wavelength is set at 605 nm, the excitation spectrum shows a strong excitation peak at 574 nm. It is noted that PTGO in hexane exhibits an absorption band at 635 nm, which is at a longer wavelength than the observed emission band. Since the film has a similar absorption band, one can conclude that the 635 nm absorption is due to non-emissive aggregates. In hexane, both the monomeric **PTG0** molecules and **PTG0** aggregates appear to be present. It is reasonable to assume that the maximum absorption wavelength of the monomeric species in hexane is around 580 nm $(\lambda_{max} \text{ of } \mathbf{PTB} \text{ in hexane is 554 nm})$. Given the resolved structured emission, the similar excitation spectra in hexane to those in chloroform, the apparent matching of the excitation spectra to the absorption of the non-aggregated monomeric species, one can conclude that the emissions observed for PTGO in hexane are due to non-aggregated PTG0 molecules. Some PTG0 aggregates do exist. Such aggregates are non-emissive and are responsible for the redshifted absorptions. Although PTGO exhibits low fluorescence quantum yields in both solvents, its hexane solution is clearly more fluorescent, presumably due to hexane's low polarity.

PTG1 shows similar absorption behavior to **PTG0**: red-shifted absorptions in hexane, which resemble those of its film (Fig. S12). Different from **PTG0** though which shows stronger emission in hexane than in chloroform, **PTG1** is non-fluorescent either in hexane or as thin films.

2.3.4. Molecular dynamics (MD) simulations. To understand the aggregation behaviors of these PDI derivatives, molecular dynamics simulations were carried out using Sander in AMBER10.0 software package³⁹ with the AMBER 99SB force field⁴⁰ and chloroform as the solvent to obtain the energy-minimized dimer structures. The starting structure of the **PRT** dimer was built and optimized with the MMFF force field using MOE program⁴¹ based on a structurally similar dimer obtained in the Cambridge Structural Database (CSD entry 4312157).⁴² The **PAT** dimer and the **PTB** dimer were built based on the PRT dimer and were minimized with the MMFF force field. Each system (PRT dimer, PAT dimer, and PTB dimer) was soaked in a rectangular box of explicit chloroform molecules extended 10 Å away in all directions from any solute atom. Each system was minimized for 1000 steps to reduce steric clash, followed by 30 ps of ramping up the temperature from 10 K to 300 K, and a 100 ps equilibration at 300 K. The equilibrated system was continued with a production run of 2000 ps, collecting 2000 snapshots with the time step of 2 fs. The 2000th ps snapshot structure for the **PRT** dimer was shown in Fig. 10A. The 2000th ps



Fig. 10. Structures of PRT dimer (A), PAT dimer (B), and PTB dimer (C) generated by molecular dynamics simulation. The PRT dimer was taken from the 2000th ps snapshot while the PAT and PTB trajectories were taken from the 500th ps. Hydrogen atoms were not shown for clarity.

snapshot structures for **PAT** and **PTB** dimers however were dissociated. We traced back the MD trajectories and found that the 500th ps snapshot structures were dimers. These two structures were minimized and reported in Fig. 10B and C for the **PAT** dimer and the **PTB** dimer, respectively. From MD simulations, one can draw three conclusions: (1) the PDI core of **PAT** forms a π – π stacking with a much larger rotational offset than that of the **PRT** dimer. (2) The **PRT** dimer structure is much more stable than the **PAT** dimer structure; while the **PRT** dimer structure was well preserved at the 2000th ps snapshot, the **PAT** dimer started to dissociate from the 600th ps, and at the 800th ps the **PAT** dimer completely dissociated. (3) There is no PDI–PDI core stacking in the **PTB** dimer as the two PDI units are nearly perpendicular to each other. These results are consistent with their fore-discussed NMR data and optical properties.

MD simulations were also carried out on **PTG0** and **PTG1**. We have previously carried out MD simulations on two ether-linked analogs **POG0** and **POG1**.³⁶ The structures of **PTG0** and **PTG1** were built based on those of **POG0** and **POG1**, respectively, followed by optimization using the MMFF force field.⁴³ As shown in Fig. 11, while the G0 or G1 unit on one side of the PDI core adopts a conformation almost perpendicular to the PDI core, the triphenylene moiety on the other side of the PDI core has a much smaller twisting angle in respect to the PDI core, enabling extended π -conjugation between the PDI core and at least one side of the triphenylene dendrons, which accounts for their red-shifted absorptions.

energetically favorable, the frontier orbitals of **PTGn** were evaluated using cyclic voltammetry measurements. The cyclovoltammograms of **PTB**, **PTG0**, **G0T**, and **G1T** scanned in chloroform solutions using a 1 mm² Pt disk as the working electrode, Ag/AgNO₃ as the reference electrode and a Pt wire as the counter electrode are shown in Fig. 12.

PDI core is fairly electron deficient and thus easy to reduce and difficult to oxidize. GOT and G1T. on the other hand, are electron rich and easy to oxidize. During cathodic scan, PTB and PTGO both show two reversible reduction waves (Fig. 12), which can be attributed to the reduction of the π -acceptor system. The first reduction potential of **PTGO** is very close to that of **PTB** (-1.04 V for PTB and -1.03 V for PTGO, vs Cp₂Fe). The stronger electron-donating nature of triphenylene's π -system (than phenyl's) would lower PDI's reduction potential (more negative potential) while the more extended π -conjugation in the **PTGO** system would raises PDI's reduction potential (less negative). The two opposite effects apparently cancel out. Based on the above potentials, the LUMO of the π -acceptor system for **PTB** and **PTG0** can be calculated to be -3.76 and -3.77 eV, respectively. On the anodic scan, **PTG0** shows two semi-reversible oxidation waves as well; at least the first can be attributed to the oxidation of the π -donor system. From the onset potential of the first oxidation process (0.82 V vs Ag/Ag⁺ or 0.38 V vs Cp₂Fe), the HOMO of the **PTGO**, which is associated with the π -donor component is estimated to be -5.18 eV. The absorption spectra of **PTGO** give bandgap energies of the two π -systems as 2.95



Fig. 11. Energy minimized structures of PTG0 (A) and PTG1 (B) generated from MD simulations.

2.3.5. Electrochemistry and photoinduced charge transfer. As discussed earlier, both PTG0 and PTG1 in chloroform are very weak fluorescent compounds with quantum yields less than 0.01. Considering the fact that **PTB** has near unity fluorescence quantum yield and G1T is also moderately fluorescent (0.30 quantum yield), fluorescence quenching is clearly efficient in both PTG0 and PTG1. While there are π -conjugation extending to both the PDI core and the attached triphenylene dendron, UV/vis absorption spectra of PTG0 and PTG1 clearly indicate the existence of two extended chromophoric π -systems, one originating from the PDI core and extending to part of G0 or G1 structure, which absorbs in the visible range and can be labeled as the π -acceptor system, and the other from the G0 or G1 extending toward the PDI core, which absorbs in the 300–450 nm range and can be called the π -donor system. To confirm whether or not a charge transfer process, following either the donor-system excitation or the acceptor system excitation, is and 2.02 eV, respectively. Coupled with CV data, the frontier orbitals for the donor (**GOT**-associated) and the acceptor (PDI associated) components are obtained as shown in Fig. 13. Due to insufficient sample, we were unable to obtain the cyclovoltammogram of **PTG1**. As a rough approximation the HOMO of **PTG1** was estimated from the oxidation potential of **G1T** (0.72 V vs Ag/Ag⁺ or 0.28 V vs Cp₂Fe), which yields a HOMO level of -5.08 eV. Similarly, the LUMO of the π -acceptor system in **PTG1** can be roughly estimated to be the same as that of **PTG0**. Combining the electronic bandgaps (2.85 and 1.95 eV) obtained in the absorption spectrum of **PTG1**, the frontier orbitals of the donor component and the acceptor component are also estimated and are shown in Fig. 13.

For both **PTG0** and **PTG1**, when the donor component is excited, one sees a facile electron transfer from excited donor to the LUMO of the acceptor, leading to a non-emissive charge-separated state.



Fig. 12. Cyclic voltammograms of PTB, PTG0 on cathodic scan (left), and PTG0, G0T, G1T on anodic scan (right). Graphs are vertically offset for clarity. Under identical conditions, the ferrocene/ferrocenium couple has a half wave potential of 0.36 V.



Fig. 13. Frontier orbitals of the donor and the acceptor components in PTGO and PTG1.

One competing pathway is the deactivation of the donor exciton through Förster energy transfer, leading to acceptor excitation, which can be subsequently quenched by charge transfer. When the acceptor component is excited, there is a facile hole-transfer pathway, which moves the hole from the HOMO of the acceptor to the HOMO of the donor, leading to the same non-emissive charge-separated state. Thus, whether the donor or the acceptor is excited, photoinduced electron (or hole) transfer follows, which quenches both the donor and the acceptor fluorescence and leads to a non-emissive photoinduced charge-separated state. Since photoinduced electron transfer is solvent polarity dependent and more polar solvent is conducive to charge separation, it is likely that the photoinduced electron transfer of **PTG0** in hexane is much less efficient than in chloroform, which accounts for its higher PDI fluorescence in hexane.

3. Conclusions

A number of groups including trimethylsilyl, phenyl, triphenylene, and triphenylene-based G1 dendron have been linked to the bay positions of a perylene diimide (PDI) core through an ethynyl linkage. The photophysical properties of the resulting baysubstituted PDI derivatives have been carefully studied in different solvents and as thin films. Without any capping group, the two ethynyl bay-substituted PDI derivatives PAT and PRT both aggregate strongly even in dilute solutions but in different perylene–perylene π – π stacking motif; **PRT** aggregates through slipped (or longitudinal) stacking while **PAT** self-assembles by rotational (or cross) stacking. With capping groups, the PDI core stacking is completely blocked for **PATS** in both solution and solid film. For PRTS, the slipped stacking is observed only for its film sample, while for PTB, association only occurs after excitation (excimer formation). When triphenylene or triphenylene-based G1 dendron is attached to the acetylene bridge, the resulting donor-acceptor systems exhibit strong electronic coupling between the dendritic donors and the PDI acceptor, leading to significantly red-shifted absorption bands. The conjugated linkage also facilitates photoinduced electron transfer from the triphenylene or triphenylene dendron to the PDI core, effectively quenching both the donor and acceptor fluorescence emissions. The significantly red-shifted absorption bands and the efficient photoinduced electron transfer observed on PTG0 and PTG1 indicate that these new PDI derivatives may find applications in solar cells.

4. Experimental section

4.1. General

All reagents and solvents were obtained from either Aldrich or Fisher and were used as received unless otherwise stated. Anhydrous THF were distilled over sodium/benzophenone. Triethylamine was distilled from calcium hydride prior to use. All air- and moisture-sensitive reactions were carried out in oven-dried glassware under a nitrogen atmosphere unless stated otherwise.

¹H and ¹³C NMR spectra were recorded on a Varian Unity 400 MHz NMR spectrometer. A Voyager DE Pro (Perceptive Biosystems/ABI) MALDI-TOF mass spectrometer was used for mass measurement, operating in reflector mode. A mixture of silver trifluoroacetate/dithranol (1,8-dihydroxyanthrone; 1:25 w/w) was used as the matrix. UV-vis absorption spectra were recorded in 1 cm path length UV-grade spectrophotometric cells using a Hewlett-Packard 8452A diode array spectrophotometer. The fluorescence emission and excitation spectra were measured using a Shimadzu RF-5301PC spectro-fluorophotometer. All samples were deoxygenated by bubbling N2 gas through the sample immediately prior to the fluorescence measurements. Fluorescence quantum yields were determined by comparing the integrated fluorescence spectra of the compounds with the integrated fluorescence spectrum of the selected standard and correcting for the different refractive indices of the sample and the standard. For GO and G1 emissions, quinine sulfate in 1 N H₂SO₄ (Φ_{fl} =0.55) was used as the standard, while cresyl violet perchlorate in methanol $(\Phi_{\rm fl}=0.54)$ was used as the standard for determining the fluorescence quantum yield of the PDI core emissions. The refractive index of the solvent was used to approximate the sample refractive index, and the refractive index of water was used for the standard (both at 25 °C). Cyclic voltammetry (CV) studies were carried out in chloroform at room temperature under argon protection using a BAS Epsilon EC electrochemical station employing a 1 mm² Pt disk as the working electrode, Ag/AgNO₃ as the reference electrode and a Pt wire as the counter electrode. 0.1 M tetrabutylammonium hexafluorophosphate was the supporting electrolyte, and the scan rate was 50 mV/s. Each measurement was calibrated with ferrocene (Fc) as the internal standard (with the measured $E_{1/2}^{FC} = 0.355V \text{ vs Ag/AgNO}_3$). In the case of reversible curves, each anodic and corresponding cathodic potential was averaged as $E_{1/2}^{\text{red/ox}} = 1/2(E_{\text{pc}} + E_{\text{pa}})$ to obtain oxidation and reduction potentials. HOMO and LUMO energy levels were estimated on the basis of the reference energy levels of ferrocene (4.8 eV below the vacuum level) according to $E_{\rm HOMO}/E_{\rm LUMO}=4.8+(E_{1/2}-E_{1/2}^{\rm FC})$ eV below the vacuum level.

4.1.1. PRTS. Regioisomeric mixture of PRBr was synthesized according to a literature procedure.⁴⁴ A mixture of 1,7- and 1,6-PRBr (0.11 g, 0.16 mmol), triisopropylsilylacetylene (0.18 mL, 0.81 mmol), Pd(PPh₃)₂Cl₂ (0.0068 g, 0.0096 mmol), CuI (0.0045 g, 0.0236 mmol), triethylamine (20 mL) was stirred under nitrogen at 90 °C for 24 h and was then poured into dichloromethane. The resulting mixture was passed through Celite. The filtrate was washed with aqueous HCl (1 N) and then with water (two times). The organic layer was separated and dried over MgSO₄. The crude product obtained by solvent evaporation was purified by chromatography on silica gel using 50% toluene in hexane as the eluent to give the product as bright red solid (0.113 g, 78%, mp 256.3 $^{\circ}$ C). ¹H NMR (400 MHz, CDCl₃): δ 10.21 (d, J=8.0 Hz, 2H), 8.71 (s, 2H), 8.51 (d, J=8.0 Hz, 2H), 4.18 (t, J=4.0 Hz, 4H), 1.75 (m, 4H), 1.45 (m, 12H), 1.21 (m), 1.19 (s, 36H), 0.89 (t, J=4.0 Hz, 6H). ¹³C NMR (400 MHz, CDCl₃): δ 163.0, 138.4, 134.0, 130.4, 127.6, 127.3, 123.0, 121.9, 119.9, 107.4, 103.8, 40.7, 31.5, 28.0, 26.8, 22.5, 18.8, 14.1, 11.3. Anal. Calcd for C₅₈H₇₄N₂O₄Si₂ C, 75.77%, H, 8.11%, N, 3.05%. Found: C, 76.13%, H, 8.04%, N, 2.95%.

4.1.2. **PRT**. To a solution of **PRTS** (0.076 g, 0.083 mmol) in THF (10 mL), a sample of TBAF (0.056 g, 0.214 mmol) was added dropwise. The mixture was stirred at room temperature for 30 min. The crude product was obtained by solvent evaporation from reaction mixture. The resulting solid was washed with methanol to give a blackish red solid (0.023 g, 45%, no melting transition observed before crosslinking onsets around 150 °C). ¹H NMR (400 MHz, CDCl₃): δ 10.00 (d, *J*=8.0 Hz, 2H), 8.79 (s, 2H), δ 8.68 (d, *J*=8.0 Hz, 2H), 4.18 (br, 4H), 3.79 (s, 2H), 1.90–0.6 (br). ¹³C NMR (400 MHz, CDCl₃): δ 162.5 (br), 128.1 (br), 58.7, 41.1 (br), 31.5, 26.7, 22.5, 14.0. Anal. Calcd for C₄₀H₃₄N₂O₄ C, 79.19%, H, 5.65%, N, 4.62%. Found: C, 77.95%, H, 6.02%, N, 4.43%.

4.1.3. PATS. PBr was synthesized according to published literature procedures.⁴⁵ A mixture of **PBr** (0.20 g, 0.23 mmol), trimethylsilylacetylene (0.17 mL, 1.17 mmol), Pd(PPh₃)₂Cl₂ (0.0117 g, 0.0167 mmol), CuI (0.004 g, 0.021 mmol), triethylamine (30 mL) was stirred under nitrogen at 60 °C for 19 h and was then poured into dichloromethane. The resulting mixture was passed through Celite. The filtrate was washed with aqueous HCl (1 N) and then water (two times). The organic layer was separated and dried over MgSO₄. The crude product obtained by solvent evaporation was purified by chromatography on silica gel using 50% CH₂Cl₂ in hexane as the eluent to give the product as bright red solid (0.13 g, 62%)no melting transition observed before decomposition starts around 300 °C). ¹H NMR (400 MHz, CDCl₃): δ 10.28 (dd, *J*=8.0 Hz, 2H), 8.92 (d, *J*=8.0 Hz, 2H), δ 8.76 (dd, *J*=8.0 Hz, 2H), 7.50 (t, *J*=4.0 Hz, 2H), 7.36 (d, J=8.0 Hz, 4H), 2.73 (m, 4H), 1.18 (m, 24H), 0.37 (s, 18H). ¹³C NMR (400 MHz, CDCl₃): δ 163.5, 163.2, 163.0, 162.8, 145.7, 145.6, 138.9, 138.6, 135.4, 134.8, 134.5, 133.9, 131.1, 130.7, 130.5, 130.3, 130.1, 129.9, 129.8, 129.7, 128.4, 127.9, 127.6, 124.1, 123.6, 123.3, 122.1, 121.8, 120.7, 120.2, 106.5, 106.3, 105.5, 105.4, 29.2, 24.0, 0.4. Anal. Calcd for C₅₈H₅₈N₂O₄Si₂ C, 77.12%, H, 6.47%, N, 3.10%. Found: C, 77.83%, H, 6.64%, N, 2.87%.

4.1.4. **PAT.** To a solution of **PATS** (0.029 g, 0.032 mmol) in THF (5 mL), a sample of TBAF in 1 M THF (0.1 mL, 0.1 mmol) was added dropwise. The mixture was stirred at room temperature for 15 min. The crude product was obtained by solvent evaporation from reaction mixture. The resulting solid was washed with methanol to give a blackish red solid (0.0125 g, 52%, no melting transition observed before crosslinking onsets around 150 °C). ¹H NMR

(400 MHz, CDCl₃): δ 10.14–9.92 (br, 2H), 9.05 (t, *J*=2.0 Hz, 2H), δ 8.97–8.80 (br, 2H), 7.50 (m, 2H), 7.34 (m, 4H), 3.48 (br), 2.71 (br), 1.17 (m). HRMS-EI, calculated for C₅₂H₄₂N₂O₄ 758.31, found 758.3145.

4.1.5. G1T. A mixture of G1OTf (0.169 g, 0.1077 mmol), trimethylsilylacetylene (0.05 mL, 0.345 mmol), Pd(PPh₃)₂Cl₂ (0.0035 g, 0.0049 mmol), CuI (0.0035 g, 0.0184 mmol), triethylamine (0.07 mL), and anhydrous DMF (10 mL) was stirred under nitrogen at 60 °C for 21 h. The product was precipitated out from the reaction mixture and collected by filtration. The resulting solid was washed with methanol to give G1-TMS as a greenish yellow solid (0.113 g, 69%). The desilylation was carried out by adding a sample of TBAF in 1 M THF (0.08 mL, 0.08 mmol) to a THF (10 mL) solution of the above greenish yellow solid (0.093 g, 0.0613 mmol). The mixture was stirred at room temperature for 45 min and was then poured into water. The organic phase was extracted with methylene chloride. The organic extracts were washed with water, dried over anhydrous MgSO₄, and evaporated in vacuo to give a crude product, which was purified by recrystallization, using CH₂Cl₂ and methanol solvent mixture to afford G1T as a greenish yellow solid (0.0832 g, 94%. No melting transition observed before crosslinking onsets around 165 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.64 (s, 1H), 8.57 (d, J=4 Hz, 2H), 8.53 (s, 1H), 8.25 (m, 4H), 8.18 (s, 1H), 7.77 (d, J=8 Hz, 2H), 7.66 (s, 1H), 7.63 (s, 1H), 7.59 (s, 1H), 7.54 (s, 1H), 7.48 (d, *I*=8 Hz, 2H), 7.41 (s, 1H), 7.12 (m, 4H), 4.24 (m, 21H), 3.52 (s, 1H), 2.04–0.71 (m, 66H). ¹³C NMR (400 MHz, CDCl₃): δ 159.0, 158.6, 158.1, 157.9, 157.8, 157.5, 131.6, 131.3, 131.2, 130.0, 129.6, 129.4, 129.3, 129.2, 129.1, 128.7, 128.5, 124.6, 124.3, 124.1, 124.0, 123.7, 123.5, 122.8, 122.1, 115.8, 115.6, 115.5, 115, 113.5, 113.4, 111.9, 107.4, 106.1, 106.0, 105.1, 104.0, 103.5, 91.5, 90.9, 90.8, 82.0, 80.4, 69.2, 69.0, 68.3, 68.2, 56.1, 31.7, 31.6, 29.5, 29.4, 25.9, 25.8, 22.7, 22.5, 14.1, 14.0. Anal. Calcd for C₉₉H₁₁₀O₉ C, 82.35%, H, 7.68%. Found: C, 82.07%, H, 7.72%.

4.1.6. **PTB**. A sample of diisopropyl amine (4 mL) was added to the mixture of **PBr** (0.02 g, 0.023 mmol), ethynylbenzene (0.007 g, 0.0685), Pd(PPh₃)₂Cl₂ (0.001 g, 0.0014 mmol), Cul (0.0005 g, 0.0026 mmol) at room temperature. The resulting mixture was stirred under nitrogen at 75 °C for overnight. The product was precipitated out from the reaction mixture and collected by filtration. The resulting solid was washed with methanol to give **PTB** as a dark red solid (0.028 g, 74%). ¹H NMR (400 MHz, CDCl₃): δ 10.22 (dd, *J*=8.0 Hz, 2H), 9.02 (d, *J*=8.0 Hz, 2H), δ 8.87 (dd, *J*=8.0 Hz, 2H), 7.67 (m, 4H), 7.47 (m, 8H), 7.37 (d, *J*=8.0 Hz, 4H), 2.77 (m, 4H), 1.20 (m, 24H). ¹³C NMR (400 MHz, CDCl₃): δ 177.8, 163.6, 145.6, 138.2, 134.8, 134.4, 131.9, 131.2, 131.0, 130.5, 129.8, 128.9, 128.4, 128.1, 127.7, 127.3, 124.2, 123.1, 122.2, 122.0, 121.2, 120.5, 98.8, 90.6, 68.0, 47.9, 29.3, 25.6, 24.0, 19.3. Anal. Calcd for C₆₄H₅₀N₂O₄ C, 84.37%, H, 5.53%, N, 3.07%. Found: C, 84.06%, H, 5.62%, N, 3.13%.

4.1.7. PTGO. A sample of triethylamine (3 mL) was added to the mixture of PBr (0.044 g, 0.0507 mmol), G0T (0.0521 g, 0.1036 mmol), Pd(PPh₃)₂Cl₂ (0.002 g, 0.0028 mmol), CuI (0.001 g, 0.0053 mmol), and DMF (3 mL) at room temperature. The resulting mixture was stirred under nitrogen at 90 °C for 24 h. The crude product obtained by solvent evaporation from reaction mixture, was dissolved in hot chloroform and was absorbed on silica gel and loaded on a column. The column was eluted with CH₂Cl₂ followed by ethyl acetate to remove impurities. The crude product absorbed on silica gel was then subjected to Soxhlet extraction for 3 days using CH₂Cl₂ to yield **PTGO** as a black solid (0.029 g, 35%, no melting transition observed before decomposition). The pure product had limited solubility in common organic solvents. ¹H NMR (400 MHz, CDCl₃): δ 11.27 (br), 9.30 (br), 9.26 (br), 9.06 (br), 7.22 (br), 7.16 (br), 6.75 (br), 6.65 (br), 4.27 (br), 1.22 (br), 1.13 (br), 0.83 (br). MALDI-TOF mass analysis: calculated for C₁₁₄H₁₁₄N₂O₁₀ 1672.13, found $[M]^+$ 1672.96, $[M+Na]^+$ 1694.94. Anal. Calcd for $C_{114}H_{114}N_2O_{10}$ C, 81.88%, H, 6.87%, N, 1.68%. Found: C, 81.37%, H, 7.02%, N, 1.76%.

4.1.8. PTG1. A sample of triethylamine (1 mL) was added to the mixture of G1T (0.035 g, 0.0242 mmol), PBr (0.010 g, 0.0115 mmol), Pd(PPh₃)₂Cl₂ (0.001 g, 0.0014 mmol), CuI (0.0007 g, 0.004 mmol), and DMF (3 mL) at room temperature. The resulting mixture was stirred under nitrogen at 90 °C for 24 h. The product was precipitated out from the reaction mixture and collected by filtration. The resulting solid was purified by chromatography eluting with THF to give the pure product as dark green solid (0.0086 g, 21%, no melting transition observed before decomposition). The pure product had limited solubility in common organic solvents. ¹H NMR (400 MHz, CDCl₃): δ 10.54 (br), 8.67 (br), 8.33 (br), 7.82 (br), 7.51 (br), 7.32 (br), 7.1 (br), 4.29 (br), 4.09 (br), 2.81 (br), 1.81 (br), 1.63 (br), 1.49 (br), 1.31 (br), 0.87 (br). MALDI-TOF mass analysis: calculated for C₂₄₆H₂₅₈N₂O₂₂ 3594.68, found [M+Ag]⁺ 3702.70. Anal. Calcd for C246H258N2O22 C, 82.19%, H, 7.23%, N, 0.78%. Found: C, 81.46%, H, 7.49%, N, 0.83%.

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Supplementary data

¹H and ¹³C NMR spectra of the compounds, MALDI-TOF mass spectra, molecular dynamics (MD) simulations, additional optical spectra (absorption, fluorescence emission, excitation). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2012.02.008.

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