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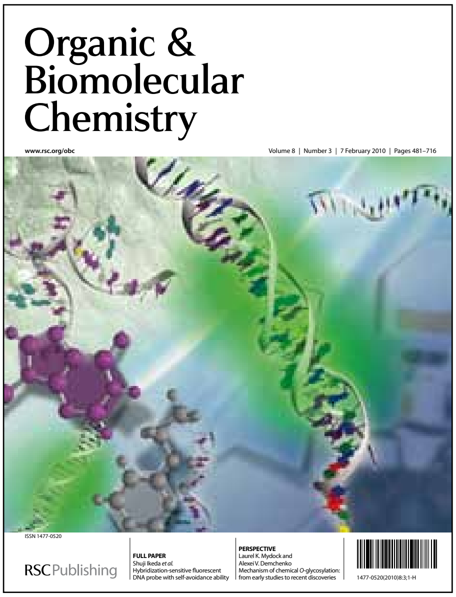

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ARTICLE TYPE

Supramolecular Assemblies of *bay*-Substituted Perylene Diimides in Solution and on Solid Substrate

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Perylene diimides (PDIs) substituted with a terpyridine moiety at the *bay*-region have been synthesized. These building blocks were used to construct supramolecular complexes in chloroform. A dimer and a trimer were built via the *bay*-region complexation with zinc. The PDI compounds were further modified to have silane anchors and PDI self-assembled monolayers (SAMs) were prepared on quartz substrate. Complexation of metal ions was also done on the surface, and this was observed clearly in the absorption spectrum. These studies on surface show possible progress towards supramolecular multilayer structures.

Introduction

In recent years, considerable attention has been focused on surface modification of solid substrates by forming highly ordered organic films. One of the approaches to form ultrathin films on the surface is immersing the substrate into a diluted solution of an anchor-containing organic compound. The formed films are referred to as self-assembled monolayers (SAMs).[1] Silanes are one of the anchor group types, which form a strong and stable covalent bond between the molecule and an oxide surface.[2] Siloxane-containing compounds are rather difficult to synthesize but they enable creating SAMs fast and easy.[3-4]

The use of a chelating ligand, such as a terpyridine, supports the formation of supramolecular assemblies. Terpyridine ligands are highly attractive terminal groups to be incorporated into SAMs, since they can coordinate to a broad range of metals and be substituted with many different functionalities.[5] The three nitrogen donors on each 2,2′:6′2″-terpyridine (tpy) interact strongly with the metal ion. Most commonly used metals for this purpose are zinc(II)[6-7] and ruthenium(III)/(II)[8]. The terpyridine moieties are widely used in metallo-supramolecular polymers, where their role is significant.[9]

Perylene diimides (PDIs) are a unique class of chromophores, which exhibit outstanding optical, electronic and physical properties. Typically, PDIs are functionalized at the imide ring, which restricts the interactions between chromophores and their successive layers.[10] On the other hand, introducing functional groups in the *bay*-region (1,6,7,12-positions) modifies the electronic and optical properties of PDIs and allows their fine tuning.[11-12] These dyes combined with the tpy units are powerful building blocks for supramolecular organization and because of their photoactive properties these units can be used for optoelectronic applications.[13-14]

In this paper we report syntheses of PDIs substituted with the terpyridine moiety at the *bay*-region. Terpyridine moieties at the *bay*-region in PDIs are extremely rare.[15] We have also synthesized PDIs with a silane anchor and prepared PDI SAMs on a solid substrate (quartz). Siloxane anchors on PDIs are also uncommon and to the best of our knowledge, no PDIs with a silane anchor at the *bay*-region have been published before.[16] Covalent attachment to the substrate was done in one step and monomolecular layer formation was proved by absorption measurements. Coordination with zinc(II) is a promising option for layer-by-layer formation of supramolecular assemblies of photoactive compounds.[17] A supramolecular dimer and a trimer were constructed in solution. Such tpy-PDI complexes, which are connected through the *bay*-region, were prepared for the first time. Furthermore, energy transfer from the middle PDI to the side PDIs was observed in the PDI trimer with quantum yield close to unity, eventhough the distance between the donor and the acceptor is quite long.

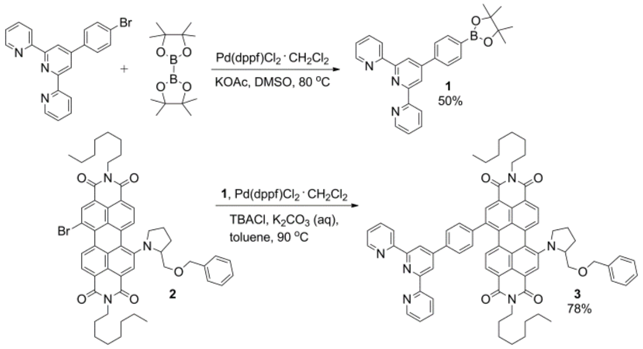
Results and Discussion

Synthesis

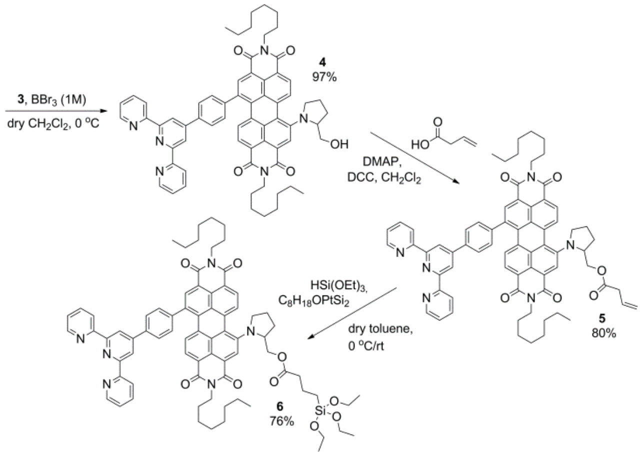
Borylation of bromophenylterpyridine was done according to Scheme 1 with a moderate yield of 50% of tpy **1**. Attempts to improve the reaction efficiency by changing the base to NaOAc and by using the catalyst $PdCl_2$ and the ligand [dppf = 1,1′-bis(diphenylphosphanyl)ferrocene] as separate reagents did not increase the yield. Tpy **1** was used in a Suzuki coupling reaction with 2-(benzyloxymethyl)pyrrolidine substituted PDI **2**. The synthesis of PDI **2** was done according to the procedure reported earlier.[18]

Building block tpy-PDI **3** was synthesized from regioisomerically pure 1,7-PDI **2** (Scheme 1).[11] The reaction was done in a toluene/water biphasic system with Pd catalyst. Product **3** was purified using automated low-pressure Combiflash chromatograph on an alumina column. Silica columns could not be used for the purification because of their excessive sorption of terpyridyl-containing compounds.

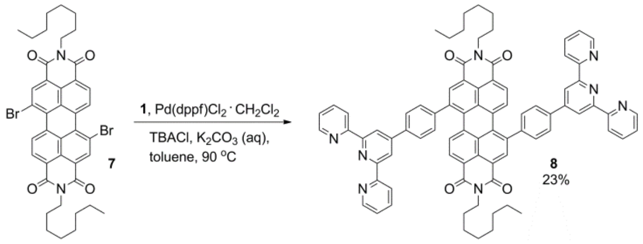
Deprotection of tpy-PDI **3** was performed using boron tribromide (Scheme 2). Thus received PDI **4** was further modified



Scheme 1 Borylation of tpy **1** and Suzuki coupling reaction of tpy-PDI **3**.



Scheme 2 Synthetic route to tpy-PDI-Si(OEt)$_3$ **6**.

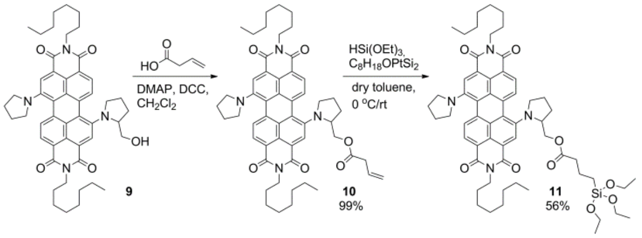


Scheme 3 Synthesis of bis(substituted) tpy-PDI **8**.

to have a siloxane anchor. The hydrosilylation procedure was similar to the one published earlier for other chromophores.[4] Compounds **4**, **5** and **6** were obtained with relatively high yields as indicated in Scheme 2.

Bis(substituted) tpy-PDI **8** (Scheme 3) was synthesized from dibromo-PDI **7**, which was pure 1,7-regioisomer.[11] The reaction conditions were similar to those described for PDI **3**. However, purification was not straightforward because of the minor amount of mono-tpy-substituted PDI. Column separation did not provide enough resolution, and the complete separation was achieved only using preparative alumina TLC plates.

Bis-pyrrolidine PDI **11** with a siloxane anchor was also prepared to compare the bonding densities of PDIs with different substituents. Hydroxy-PDI **9** was prepared according to the literature procedure.[18] Syntheses of allyl PDI **10** and siloxane PDI **11** were similar as for the terpyridine PDIs. Purification of all these compounds could be efficiently performed using silica gel. The synthetic route is presented in Scheme 4.



Scheme 4 Synthetic route to pyr-PDI-Si(OEt)$_3$ **11**.

Solution studies

PDIs **3** and **8** were used to construct supramolecular complexes in solution. According to the literature, zinc ion forms complexes with terpyridine under very mild conditions and the complexation can be detected from their absorption spectra.[7, 13] In our experiments, zinc acetate did not give stable complexes. Therefore, the counter ion was changed and zinc triflate (Zn(OTf)$_2$) was chosen. The complexes were prepared by dissolving PDI (**3** or **8**) in CHCl$_3$/CH$_3$CN and adding zinc triflate stock solution in the mixture. The reaction solution was stirred at room temperature for 1h. Structures of the formed zinc complexes **Zn-3** and **Zn-8** are presented in Figure 1.

A dimer (**3-Zn-3**) and a trimer (**3-Zn-8**) were also prepared (Figure 1). The dimer was produced either from monomers **Zn-3** and **3** (**3-Zn-3a**) or directly from PDI **3** (**3-Zn-3b**). Trimer **3-Zn-8** was assembled in DMF because the solubility of **Zn-8** in chloroform-based solvents was poor.

Steady-state absorption was used as a quick method to prove the formation of the complexes. Characteristic absorption bands of tpy-PDI **3** appear between 550-750 nm and 400-500 nm (Figure 2). Both the PDI core and the tpy unit absorb also at the wavelengths below 350 nm. The 650 nm centered band is characteristic for pyrrolidine substituted PDI.[19] Distinct changes in absorption were observed after complexation with zinc: an increase of the absorption intensity between 300-350 nm and a decrease and sharpening around 270 nm. These correspond to the changes in the tpy unit absorption and thus indicate the formation of the zinc complex.[13]

Table 1. Absorption and emission maxima of compounds **3** and **8** and their zinc complexes in CHCl$_3$.

Compound	Absorption, λ_{max} (nm)	Emission, λ_{max} (nm)
3	284, 442, 662	753
Zn-3	288, 397, 438, 663	757
3-Zn-3a	288, 402, 439, 666	758
3-Zn-3b	288, 403, 442, 666	759
8	284, 556	619
Zn-8	288, 338, 553	607
3-Zn-8	288, 389, 439, 666	603, 755

Small red-shift of the absorption maximum of the PDI unit from 662 nm to 666 nm was observed during the complexation. Also in the emission spectra a small shift of the maximum was noticed (Figure 3). The two-fold increase in the molar absorptivities (ε) were observed for the dimers (**3-Zn-3a** and **3-Zn-3b**). As expected, the dimers formed via different routes give identical absorption spectra (Figure 2). Table 1 presents absorption and emission maxima of compounds **3** and **8** and their complexes in solution.

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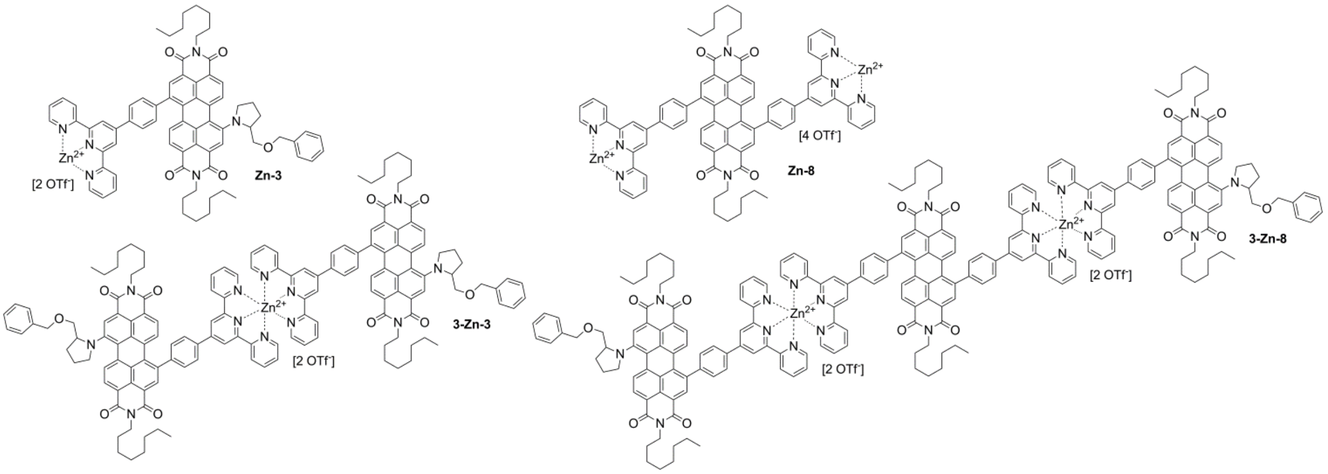

Fig. 1 Supramolecular complexes.

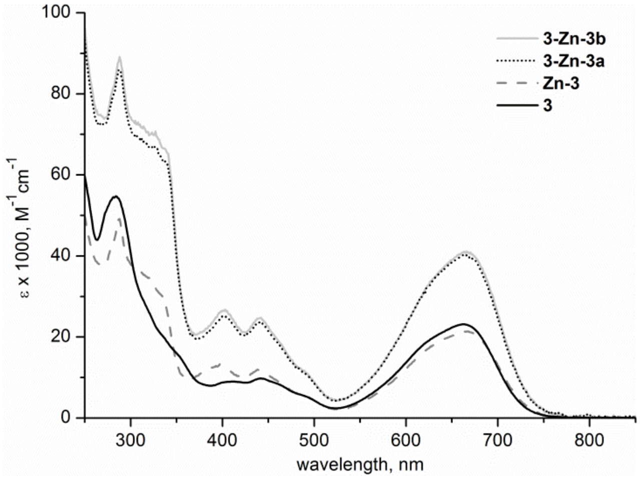

Fig. 2 Absorption spectra of tpy-PDI **3** and its zinc complexes in $CHCl_3$.

Zn-complexation of compound **8** showed similar changes in the absorption spectrum as that of compound **3**, i.e. an increase of the absorption around 340 nm and sharpening below 300 nm, which are due to the formation of zinc tpy (**Zn-8**, Figure 4). Remarkable blue shift was observed for the PDI band from around 660 nm of **3** and **Zn-3** to around 555 nm of **8** and **Zn-8**. Such shift was expected for PDI **8** where there is no pyrrolidine substituent. The low molar absorptivity of **Zn-8** in Figure 4 can not be considered accurate because of low solubility and aggregation of the complex in $CHCl_3$. When trimer **3-Zn-8** was formed, bands similar as for **3** and **Zn-3** were spotted and the absorption maxima match well with the zinc complexes of PDI **3** and **8** (Table 1). Evidently the shoulder at about 570 nm corresponds to the PDI moiety between the two tpy units (**8**), and the maximum at about 665 nm to the PDI complexed with only one tpy moiety (**3**).

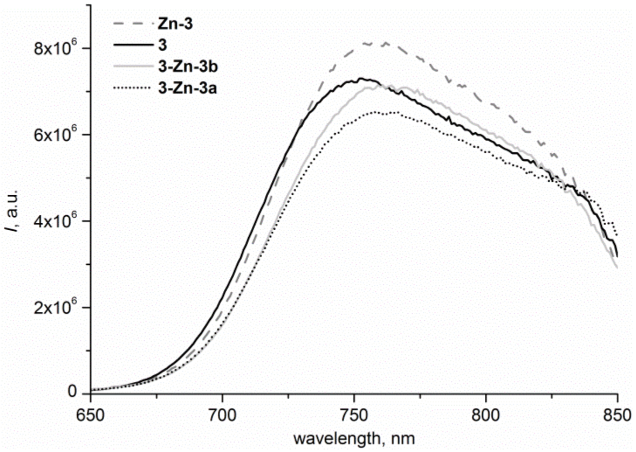

Fig. 3 Emission spectra of tpy-PDI **3** and its zinc complexes in $CHCl_3$ (Exc: 630 nm).

The emission spectra of bis(substituted) tpy-PDI **8** and its zinc complexes are presented in Figure 5. As expected, the spectrum of trimer **3-Zn-8** has two emission maxima at 603 nm and 755 nm, which correspond to PDI **8** and PDI **3**, respectively. Quenching of the fluorescence bands around 600 nm and 760 nm are seen in the trimer, whose emission spectrum is multiplied by 25 for comparison with the references. At the excitation wavelength of 505 nm absorbance of PDI **3** is rather weak in comparison to that of PDI **8**, but still relatively strong emission around 750 nm is observed for the trimer. This indicates that energy transfer from the middle PDI to one of the side PDIs is the reason for the quenching in the trimer.

Energy transfer from the middle PDI to the side PDI was confirmed by time-resolved fluorescence measurements with the time-correlated single photon counting method. Lifetimes of the first singlet excited state of reference compounds PDI **8** and PDI **3** were determined as 8.3 ns and 1.57 ns, respectively (see

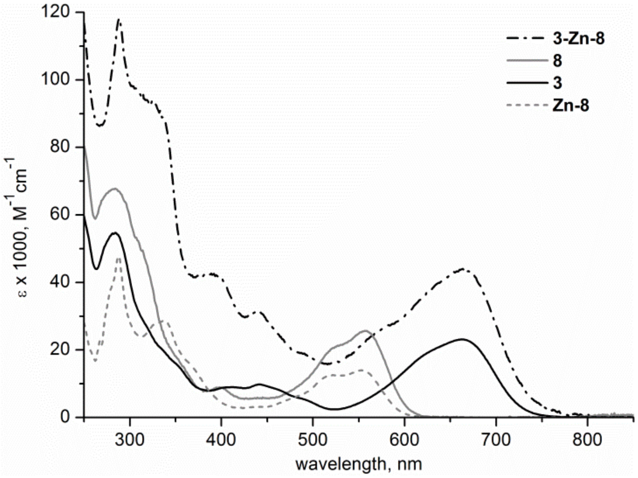

Fig. 4 Absorption spectra of bis(substituted) tpy-PDI **8** and its zinc complexes in $CHCl_3$. The absorption spectrum of tpy-PDI **3** is shown for comparison.

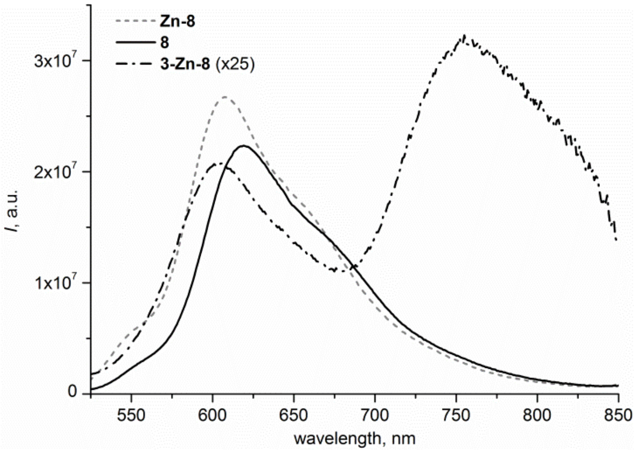

Fig. 5 Emission spectra of bis(substituted) tpy-PDI **8** and its zinc complexes in $CHCl_3$ (Exc: 505 nm).

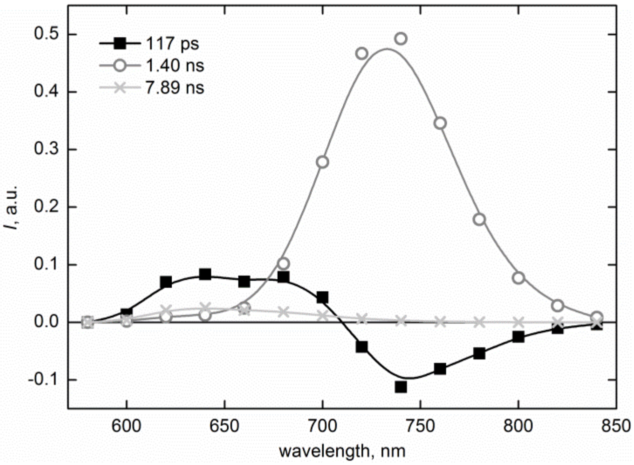

Fig. 6 Fluorescence decay-associated spectra of trimer **3-Zn-8** in $CHCl_3$ (Exc: 405 nm).

Supporting Information). To distinguish between the different emitting species in **3-Zn-8**, fluorescence decays were collected with a constant accumulation time (180 s) in the range 580-840 nm with 20 nm steps. The obtained decay curves were fitted globally to obtain fluorescence decay component spectra (Figure 6). Three exponents were needed for a reasonable fit quality. The fastest component (117 ps) follows the shape and position of the fluorescence spectrum of PDI **8** at 600-700 nm. The negative amplitude around 750 nm indicates a formation of fluorescence and thus corresponds to energy transfer from the middle PDI to the side PDI. The formed component shows clearly the spectrum of PDI **3** (see Figure 6) centered at 750 nm and the lifetime (1.40 ns) is in agreement with the one measured for reference PDI **3** (1.57 ns). The final component with a lifetime of 7.89 ns is weak in amplitude, but shows clearly the spectrum of PDI **8**. The lifetime is similar to that measured for reference PDI **8** and this component can be assigned to a small amount of free PDI **8** in the solution due to dissociation of the trimer.

The rate constant of energy transfer, k_{enT}, in the trimer can be calculated as $k_{\mathrm{enT}} = k_1 - k_{\mathrm{fl}}$, where k_1 is the rate constant of the fastest process in the trimer (8.55×10^9 s^{-1}) and k_{fl} is the rate constant of the fluorescence, which is obtained from the measurement of PDI **8** (1.2×10^8 s^{-1}). The calculated $k_{\mathrm{enT}} = 8.43 \times 10^9$ s^{-1} and the quantum yield of energy transfer can be estimated from $\phi_{\mathrm{enT}} = k_{\mathrm{enT}} / (k_{\mathrm{enT}} + k_{\mathrm{fl}})$ as 0.99. Considering the highly efficient energy transfer, it seems unreasonable that there is significant emission around 600 nm in the steady state fluorescence spectrum of the trimer (Figure 5). This can be explained by the presence of ca. 4% (as derived from the fluorescence quenching) of the highly emissive longer oligomers[13], residual 3-Zn-3 and trimer dissociated to its components. Even a small amount of free PDI 8 will cause a strong signal in the steady state spectrum due to the relatively long lifetime of its singlet excited state.

NMR Characterization

The synthesized compounds were fully characterized by mass spectrometry (see Experimental Section) and NMR spectroscopy (see Supporting Information). All the products had good solubility allowing the NMR measurements in $CDCl_3$. The signal assignments are based on two-dimensional NMR spectroscopy, the heteronuclear single-quantum coherence (gHSQC) with multiplicity editing and the homonuclear correlation spectroscopy (COSY).

The assignment of ^{1}H NMR peaks is complicated due to the overlapping of the peaks and crowded aromatic and aliphatic regions. Thus most of the signals are visible as multiplets. However, the assignment for all the proton signals was succesfully done. When comparing the aromatic regions of compounds **3**, **4**, **5** and **6**, some small changes of peak positions are observed in the perylene core proton signals (7, 11, 14) and in the signals of phenylene protons. In the spectrum of PDI **4** these signals are distinguished better. In the spectra of PDIs **5** and **6**, the signal from proton 13 is shifted to lower field compared to the other spectra. The aliphatic regions in the spectra are quite consistent. In the spectrum of PDI **4**, the signal from proton *d* is moved to higher field when compared to the other spectra. In the spectra of PDIs **5** and **6**, the signal from proton *e* is deshielded (δ 4.66-4.41 ppm), which is due to changes in the anchor group. All the characteristic proton signals such as hydroxyl group, terminal double bond and silane protons, are observed easily from the spectra of PDIs **4**, **5** and **6**, respectively. Positions of these signals correspond well with values of previously studied chromophores.[4]

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The symmetric structure of PDI **8** makes its spectrum quite straightforward to resolve. Also the spectra of PDIs **10** and **11** are simpler than those of the other PDIs because of the uncomplicated substituent. Comparing ^{1}H NMR spectra of compounds **10** and **11**, all the peaks in the aromatic region have shifted a bit downfield in the spectrum of PDI **11**. In the aliphatic region, the signals from the terminal double bond have vanished and the silane signals are visible in the spectrum of PDI **11**. The signal positions match well with the signals in the spectrum of PDI **6**.

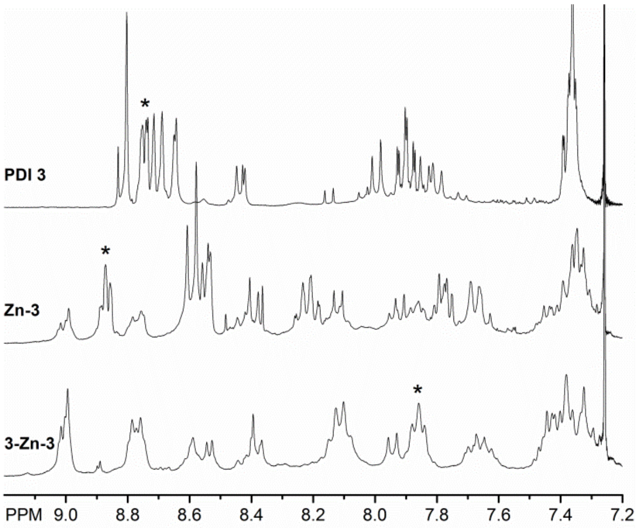

Fig. 7 The aromatic regions of ^{1}H NMR spectra of tpy-PDI **3**, **Zn-3** and **3-Zn-3**. The marked signal (*) corresponds to protons 6″-H; the closest protons to nitrogen atoms in terpyridine.

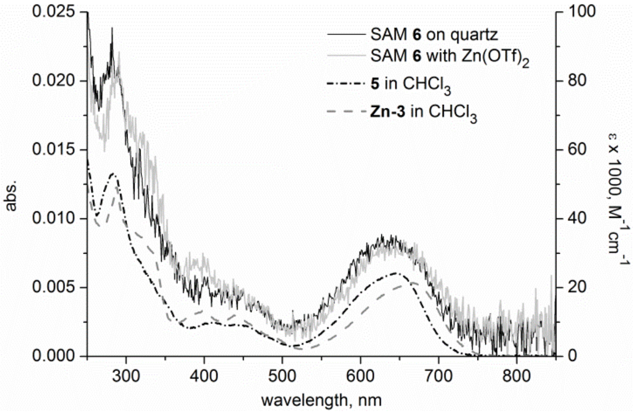

Fig. 8 Absorption spectra of tpy-PDI **5** and complex **Zn-3** on molar absorptivity (*ε*) scale and PDI SAM **6** on quartz surface.

Resolving the spectra of complexes (**Zn-3**, **3-Zn-3**, **Zn-8**, **3-Zn-8**) is complicated but possible. The signals in the aliphatic region correlate nicely with the uncomplex ones, though the aromatic region signals are shifted. When comparing the spectra of PDI **3** and complex **Zn-3**, it is clear that complexation has occurred (Figure 7). Nearly all the peaks in the aromatic region have moved in the spectrum of **Zn-3**. The closest protons to the nitrogen atoms in the terpyridine moiety (5″-H, 6″-H) are shifted to lower field from 7.35 and 8.75 ppm to 7.80 and 8.90 ppm, respectively. When comparing the spectra of **Zn-3** and dimer **3-Zn-3**, an extreme high-field shift of protons 6″-H is observed (marked with * in Figure 7). The signal from protons 5″-H is shifted back to its old position (around 7.40 ppm) in the spectrum of the dimer. These observations are similar with the results found previously for a PDI with terpyridines at the imide region.[13]

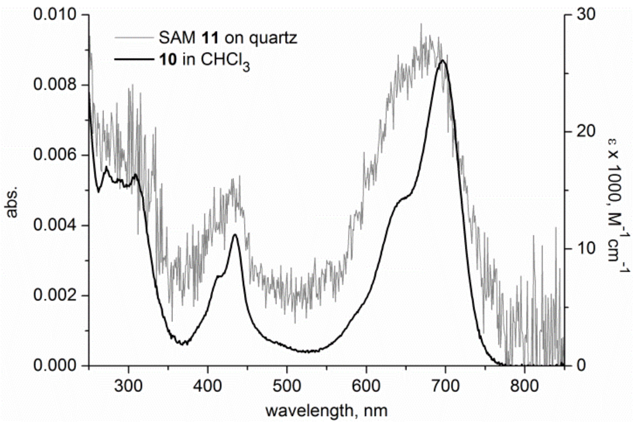

Fig. 9 Absorption spectra of pyr-PDI **10** on molar absorptivity (*ε*) scale and PDI SAM **11** on quartz surface.

Complex **Zn-8** was the only one measured in deuterated methanol because of its low solubility in $CDCl_3$. However, similar shifting of signals from protons 5″-H and 6″-H are observed when the spectra of bis(substituted) tpy-PDI **8** and **Zn-8** are compared. The signal of protons 6″-H is deshielded from 8.70 to 8.95 ppm, and the signal of protons 5″-H is shifted from 7.40 to 7.95 ppm. Assignment of the aromatic region protons in the spectrum of trimer **3-Zn-8** is too complex. The region is nearly one big multiplet. Nevertheless, the integrals match well with the number of protons.

Immobilization and Complexation

SAMs were prepared in a one-step process, where the reaction vessel was loaded with a solution of siloxane PDI **6** or **11** in distilled toluene and isopropyl amine under argon. Quartz plates were precleaned according to the previously reported method.[4] The cleaned plates were immersed in the solution, and the reaction vessel was heated at 105 °C. After 2h, the plates were sonicated on ultrasonic bath to remove residual physisorbed compound. Absorption spectra of the SAMs were obtained by subtracting the absorbance of the clean substrate from the absorbance of the plate with the SAM. Considering the absorption spectrum of the monolayer on the surface, the optical densities in Figures 8 and 9 should be divided by two, because layers are formed on both sides of the substrate.

The absorption spectrum of SAM **6** shows similar shape as PDI **5** in solution (Figure 8). Even though absorptions of the SAMs are low, the complexation with zinc triflate is nicely observed from the spectrum of the plate. Complexation on the surface was done by immersing the substrate with the SAM in the salt solution for 1h. Same changes in the absorption spectrum are seen as with complexation in chloroform: an increase of absorption between 300-350 nm and a decrease around 270 nm. An expected increase at 400 nm and 440 nm is also noticeable as these bands are more intense in the complex form of PDI (absorption spectrum of **Zn-3**). The PDI band of SAMs around 640 nm is slightly red-shifted upon complexation as was visible also in the solution studies. The absorption maxima are collected

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in Table 2.

Bis-pyrrolidine PDI **11** was also attached on the surface. The absorption spectrum of SAM **11** imitates nicely the absorption of pyr-PDI **10** (Figure 9). The absorption bands are broader in the spectrum of the SAM but the band maxima correspond quite well with pyr-PDI **10** in solution (Table 2).

The absorption maximum provides a possibility to estimate the mean molecular area (mma) of the PDI in the SAM. The mma values were calculated assuming the same molar absorptivity (ε) of compounds in SAMs as in solution (Table 2). This is true only if the molecules are randomly oriented on the surface and if the chromophore-chromophore or chromophore-surface interactions are disregarded.[20] The mma values are smaller than what one could expect for perfect monolayers. This might be due to the long linker, which allows chromophores to stack one over another instead of forming an ideal monomolecular film. This hypothesis is supported by the complete fluorescence quenching of the films, which is due to the aggregation of the PDI units. Evidently, a more rigid tether is needed to improve the orientation of the molecules in films, and this research is currently under way.

Table 2. Absorption maxima and mean molecular areas (mma) of samples.

Sample	Solvent/ substrate	Absorption, λ_{max} (nm)	mma[a], (nm^2)
PDI 5	$CHCl_3$	283, 412, 647	
SAM 6	quartz	282, 640	1.01
SAM 6, Zn	quartz	291, 645	0.89
PDI 10	$CHCl_3$	272, 434, 696	
SAM 11	quartz	432, 680	0.96

[a] mma = $\varepsilon/(N_A A)$, where ε is molar absorptivity, N_A is the Avogadro constant and A is absorbance of the layer.

Experimental

Materials and instrumentations

All reagents and solvents (HPLC grade) were purchased from Sigma-Aldrich Co., Tokyo Chemical Industry Co. or VWR International. Unless otherwise mentioned, chemicals were used as received. Dichloromethane was distilled over P_2O_5 and toluene over sodium shots. Quartz plates were purchased from Finnish Specialglass.

The monitoring of reactions was carried out by thin layer chromatography (TLC), employing aluminum sheets precoated with silica gel 60 F_{254} or aluminium oxide 60 F_{254} neutral (Merck). The purification and isolation of the products was performed by column chromatography on Silica 60 (mesh size 40-63 µm) or by flash chromatography using CombiFlash Companion (Teledyne ISCO).

The ^{1}H NMR spectra were measured on Varian Mercury 300 MHz spectrometer (Varian Inc.). All chemical shifts are given in ppm relative to TMS as internal standard and the coupling constants, *J*, are given in Hz. Mass spectra were recorded on high resolution ESI-TOF LCT Permier XE mass spectrometer (Waters Corp.). The sample of an analyte was dissolved in appropriate solvent at concentration ca. 0.01 mg/mL and infused at 15 µL/min rate. The reference solution of Leucine Enkephaline (50 pg/mL) was infused simultaneously. The original spectra were centred, and lock mass TOF correction was applied. Absorption spectra were measured using Shimadzu UV-2501PC UV-Vis Recording spectrometer and emission spectra were recorded by Fluorolog Yobin Yvon-SPEX spectrofluorometer.

Fluorescence decays of the samples in the nanosecond and sub-nanosecond time scales were measured using a time-correlated single photon counting (TCSPC) system (PicoQuant GmBH) consisting of PicoHarp 300 controller and PDL 800-B driver. The samples were excited with the pulsed diode laser head LDH-P-C-405B at 404 nm and fluorescence decays were measured at the wavelength of maximum emission (620 nm and 750 nm for PDI **8** and PDI **3**, respectively). The signals were detected with a micro channel plate photomultiplier tube (Hamamatsu R2809U). The time resolution of the TCSPC measurements was about 80 ps (FWHM of the instrument response function). For trimer **3-Zn-8** the fluorescence decays were measured in a range of wavelengths 580-840 nm with a 20 nm step and constant accumulation time of 180 s. The decays at different wavelengths were fitted globally to obtain decay-associated spectra.

4'-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2':6',2''-terpyridine (1)[21]

4'-(4-Bromophenyl)-2,2':6',2"-terpyridine (100 mg, 0.26 mmol) and KOAc (76 mg, 0.77 mmol) were dissolved in DMSO (5mL) on ultrasonic bath. Bis(pinacolato)diboron (78 mg, 0.31 mmol) and Pd(dppf)$Cl_2 \cdot CH_2Cl_2$ (10 mg, 0.013 mmol) were added and the reaction mixture was stirred at 80 °C under argon for 45 min. The solution was diluted with $CHCl_3$ and washed with a saturated solution of EDTA (3 × 80 mL). The organic phase was evaporated under reduced pressure. The crude product was purified on Combiflash chromatograph using alumina column (12 g) eluting with hexane/EtOAc gradient (flow rate: 30 mL/min; hexane (1 min), hexane to hexane/EtOAc 10:3.5 (5 min), hexane/EtOAc 10:3.5 (3 min)). Product **1** was isolated as a white solid (56 mg, 50%). δ_H(300 MHz; $CDCl_3$; Me_4Si): 1.39 (12H, s, Me), 7.33-7.40 (2H, m, 5″-H), 7.89 (2H, td, *J* 7.8, 1.8, 4″-H), 7.92-7.98 (4H, m, phenylene-H), 8.68 (2H, d, *J* 7.9, 3″-H), 8.74 (2H, d, *J* 3.8, 6″-H), 8.75 (2H, s, 3′-H). δ_C(75 MHz; $CDCl_3$; Me_4Si): 25.1 (CH_3), 84.2 (C-dioxaborolane), 119.1 (C-3′), 121.6 (C-3″), 124.1 (C-5″), 126.8 (C^o-phenylene), 135.6 (C^m-phenylene), 137.1 (C-4″), 141.2 (C^i-phenylene), 149.4 (C-6″), 150.3 (C-4′), 156.2 (C-2′), 156.4 (C-2″); C^p-phenylene signal was not observed. MS (ESI-TOF, CH_3CN): *m/z* = 435.2223 $[M+H]^+$ (calcd. for $C_{27}H_{26}BN_3O_2$ 435.2233).

5-(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)-12-(2-((benzyloxy)methyl)pyrrolidin-1-yl)-2,9-dioctylanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (3)

Monobromo-PDI **2** [5-(2-((benzyloxy)methyl)pyrrolidin-1-yl)-12-bromo-2,9-dioctylanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone][18] (110 mg, 0.12 mmol), compound **1** (60 mg, 0.14 mmol), tetrabutylammonium chloride (7 mg, 0.025 mmol) and Pd(dppf)$Cl_2 \cdot CH_2Cl_2$ (10 mg, 0.012 mmol) were dissolved in a two-phase mixture of toluene (5 mL) and 1M K_2CO_3 (aq) (5 mL). The reaction mixture was stirred at 90 °C for 19 h. The organic phase was separated and washed with water (2 × 40 mL). The aqueous phase was extracted with toluene (2 × 10 mL) and the organic layers were combined and evaporated under

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reduced pressure. The product was purified on Combiflash chromatograph using alumina column (12 g) eluting with $CHCl_3$/hexane gradient (flow rate: 30 mL/min; $CHCl_3$/hexane 1:1 (6 min)). Product **3** was crystallized on a watch glass and obtained as a dark green solid (108 mg, 78%). UV-vis λ_{max}($CHCl_3$)/nm 284 (ε/dm^3 mol^{-1} cm^{-1} 54740), 442 (9800) and 662 (23120). δ_H(300 MHz; $CDCl_3$; Me_4Si): 0.81-0.93 (6H, m, 22-H), 1.18-1.54 (20H, m, 17-21-H), 1.65-1.86 (4H, m, 16-H), 1.95-2.15 (2H, m, b-H), 2.16-2.41 (2H, m, c-H), 3.43-3.77 (2H, m, a-H), 3.77-4.11 (2H, m, e-H), 4.12-4.30 (4H, m, 15-H), 4.59-4.69 (2H, m, f-H), 4.69-4.80 (1H, m, d-H), 7.32-7.41 (7H, m, 5″-H, g-H), 7.80 (1H, d, *J* 8.5, 13-H), 7.82-7.95 (5H, m, 4″-H, phenylene-H), 8.00 (2H, d, *J* 8.2, 6-H, phenylene-H), 8.39-8.48 (1H, m, 14-H), 8.62-8.67 (2H, m, 7-H, 11-H), 8.70 (2H, d, *J* 7.9, 3″-H), 8.73-8.77 (2H, m, 6″-H), 8.80 (2H, s, 3′-H), 8.83 (1H, s, 4-H). MS (ESI-TOF, CH_3CN): *m/z* = 1111.5450 $[M+H]^+$ (calcd. for $C_{73}H_{70}N_6O_5$ 1111.5486).

5-(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)-12-(2-(hydroxymethyl)pyrrolidin-1-yl)-2,9-dioctylanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (4)

Compound **3** (98 mg, 0.09 mmol) was dissolved in dry CH_2Cl_2 (5 mL) and stirred in an ice bath under a drying tube for 1 h. BBr_3 (1M solution in CH_2Cl_2; 105 µL, 0.105 mmol) was added in five different portions with an interval of 30 min. The progress of the reaction was closely monitored by TLC analysis. After complete consumption of the starting material (4 h), the reaction was quenched by addition of MeOH (10 mL). The reaction mixture was washed with water (3 × 40 mL) and the organic phase was evaporated under reduced pressure. The crude product was purified on Combiflash chromatograph using alumina column (12 g) eluting with $CHCl_3$ (flow rate: 30 mL/min). Product **4** was isolated as a dark green solid (87 mg, 97%). δ_H(300 MHz; $CDCl_3$; Me_4Si): 0.78-0.94 (6H, m, 22-H), 1.17-1.52 (20H, m, 17-21-H), 1.69-1.82 (4H, m, 16-H), 1.83-2.06 (2H, m, b-H), 2.06-2.42 (2H, m, c-H), 2.89 (1H, br s, OH), 3.42-3.68 (2H, m, a-H), 3.78-4.08 (2H, m, e-H), 4.09-4.32 (4H, m, 15-H), 4.47-4.66 (1H, m, d-H), 7.32-7.41 (2H, m, 5″-H), 7.54 (1H, d, *J* 7.9, 13-H), 7.62-7.71 (2H, m, phenylene-H), 7.85-7.94 (3H, m, 4″-H, phenylene-H), 7.99 (2H, d, *J* 8.2, 6-H, phenylene-H), 8.33-8.39 (1H, m, 7-H), 8.48 (1H, s, 11-H), 8.54 (1H, d, *J* 7.9, 14-H), 8.65-8.70 (2H, m, 3″-H), 8.70-8.75 (2H, m, 6″-H), 8.77 (2H, s, 3′-H), 8.81 (1H, s, 4-H). MS (ESI-TOF, CH_3CN): *m/z* = 1021.5068 $[M+H]^+$ (calcd. for $C_{66}H_{64}N_6O_5$ 1021.5016).

(1-(12-(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)-2,9-dioctyl-1,3,8,10-tetraoxo-1,2,3,8,9,10-hexahydroanthra[2,1,9-def:6,5,10-d'e'f']diisoquinolin-5-yl)pyrrolidin-2-yl)methyl but-3-enoate (5)

Compound **4** (75 mg, 0.073 mmol) was dissolved in CH_2Cl_2 (5 mL). DCC (30 mg, 0.15 mmol), DMAP (4 mg, 0.03 mmol) and 3-butenoic acid (12.5 µL, 0.15 mmol) were added to the solution, and the mixture was stirred at room temperature for 3.5 h. The solvent was evaporated under reduced pressure. The crude product was dissolved in a few milliliters of EtOAc, the flask was frozen under cold water and filtered through a cotton plug. This procedure was done twice. The product was purified on Combiflash chromatograph using alumina column (12 g) eluting with $CHCl_3$ (flow rate: 30 mL/min) and second purification using $CHCl_3$/CH_2Cl_2 gradient ($CHCl_3$/CH_2Cl_2 1:1 to $CHCl_3$ (6 min)). Product **5** was crystallized on a watch glass and obtained as a dark green solid (64 mg, 80%). UV-vis λ_{max}($CHCl_3$)/nm 283 (ε/dm^3 mol^{-1} cm^{-1} 53130), 412 (9870) and 647 (24310). δ_H(300 MHz; $CDCl_3$; Me_4Si): 0.80-0.94 (6H, m, 22-H), 1.19-1.52 (20H, m, 17-21-H), 1.62-1.85 (4H, m, 16-H), 1.86-2.11 (2H, m, b-H), 2.12-2.46 (2H, m, c-H), 3.22 (2H, d, *J* 6.7, $COCH_2$), 3.40-3.75 (2H, m, a-H), 4.06-4.33 (4H, m, 15-H), 4.48-4.66 (2H, m, e-H), 5.14-5.28 (2H, m, CH=C*H*$_2$), 5.86-6.05 (1H, m, C*H*=CH_2), 4.75 (1H, br s, d-H), 7.32-7.41 (2H, m, 5″-H), 7.77-7.84 (1H, m, phenylene-H), 7.85-7.93 (5H, m, 4″-H, 13-H, phenylene-H), 7.98 (2H, d, *J* 8.2, 6-H, phenylene-H), 8.50-8.71 (5H, m, 3″-H, 7-H, 11-H, 14-H), 8.71-8.76 (2H, m, 6″-H), 8.78 (2H, s, 3′-H), 8.81 (1H, s, 4-H). MS (ESI-TOF, CH_3CN): *m/z* = 1088.5270 $[M]^+$ (calcd. for $C_{70}H_{68}N_6O_6$ 1088.5200).

(1-(12-(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)-2,9-dioctyl-1,3,8,10-tetraoxo-1,2,3,8,9,10-hexahydroanthra[2,1,9-def:6,5,10-d'e'f']diisoquinolin-5-yl)pyrrolidin-2-yl)methyl 4-(triethoxysilyl)butanoate (6)

All the glassware was dried in oven (150 °C, 2 h) before use. The reaction flask was sealed with a septum, placed on an ice bath, and kept under constant argon flow. Compound **5** (15 mg, 0.014 mmol) was dissolved in distilled toluene (1 mL) and added to the flask. Triethoxysilane (0.46 mL, 2.5 mmol) and Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Pt ~2%) in xylene; 17.2 µL, 2.07 µmol) were added, and the mixture was stirred in cold under argon. After 10 min, argon was removed and after 1 h the stirring was continued at room temperature for 3 h more. The crude product was evaporated under reduced pressure using a mechanical vacuum pump. Purification was done on Combiflash chromatograph using an alumina column (12 g, purged with argon) eluting with $CHCl_3$/EtOH gradient (flow rate: 30 mL/min; $CHCl_3$ (0.5 min), $CHCl_3$/EtOH 10:1 (2 min)). Product **6** was obtained as a dark green solid (13 mg, 76%). δ_H(300 MHz; $CDCl_3$; Me_4Si): 0.51-0.71 (2H, m, COC_2H_4C*H*$_2$Si), 0.82-0.92 (6H, m, 22-H), 1.13-1.49 (29H, m, 17-21-H, Si(OCH_2C*H*$_3$)$_3$), 1.65-1.86 (6H, m, 16-H, $COCH_2$C*H*$_2$$CH_2$Si), 1.88-2.31 (4H, m, c-H, b-H), 2.33-2.53 (2H, m, COC*H*$_2$$C_2H_4$Si), 3.64-3.91 (8H, m, Si(OC*H*$_2$$CH_3$)$_3$, a-H), 4.11-4.31 (4H, m, 15-H), 4.41-4.64 (2H, m, e-H), 4.77 (1H, br s, d-H), 7.34-7.41 (2H, m, 5″-H), 7.78-7.83 (1H, m, phenylene-H), 7.85-7.98 (5H, m, 4″-H, 13-H, phenylene-H), 8.03 (2H, d, *J* 8.2, 6-H, phenylene-H), 8.52-8.72 (5H, m, 3″-H, 7-H, 11-H, 14-H), 8.72-8.77 (2H, m, 6″-H), 8.80 (2H, s, 3′-H), 8.83 (1H, s, 4-H). MS (ESI-TOF, CH_3CN): *m/z* = 1253.6212 $[M+H]^+$ (calcd. for $C_{76}H_{84}N_6O_9Si$ 1253.6147).

5,12-bis(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)-2,9-dioctylanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (8)

1,7-Dibromo-PDI **7** [5,12-dibromo-2,9-dioctylanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone][11, 19] (50 mg, 0.06 mmol), compound **1** (62 mg, 0.14 mmol), tetrabutylammonium chloride (4 mg, 0.013 mmol) and Pd(dppf)Cl_2·CH_2Cl_2 (11 mg, 0.013 mmol) were dissolved in a two-phase mixture of toluene (5 mL) and 1M K_2CO_3 (aq) (5 mL). The reaction mixture was stirred at 90 °C for 18 h. The organic phase was separated and washed with water (2 × 30 mL). The aqueous phase was extracted with toluene (2 × 10 mL) and the organic layers were combined and evaporated under reduced pressure. The product was purified on preparative TLC plate (aluminium oxide), eluent CH$_2$Cl$_2$/CHCl$_3$ 2:1. Product **8** was obtained as the second fraction (R_f = 0.4 in CH$_2$Cl$_2$/CHCl$_3$ 2:1) as a dark red solid (19 mg, 23%). UV-vis λ_{max}(CHCl$_3$)/nm 284 (ε/dm^3 mol^{-1} cm^{-1} 67790) and 556 (25610). δ_H(300 MHz; CDCl$_3$; Me$_4$Si): 0.78-0.95 (6H, m, 22-H), 1.16-1.50 (20H, m, 17-21-H), 1.65-1.85 (4H, m, 16-H), 4.02-4.29 (4H, m, 15-H), 7.33-7.45 (4H, m, 5″-H), 7.62 (2H, d, *J* 7.3, phenylene-H), 7.74 (2H, d, *J* 7.3, phenylene-H), 7.86-7.98 (6H, m, 4″-H, 6-H, 13-H), 8.01-8.11 (4H, m, phenylene-H), 8.15-8.26 (2H, m, 7-H, 14-H), 8.65-8.79 (10H, m, 3″-H, 6″-H, 4-H, 11-H), 8.80-8.87 (4H, m, 3′-H). MS (ESI-TOF, CHCl$_3$/MeOH 10:15): *m/z* = 1229.5481 [M+H]$^+$ (calcd. for C$_{82}$H$_{68}$N$_8$O$_4$ 1229.5442).

(1-(2,9-dioctyl-1,3,8,10-tetraoxo-12-(pyrrolidin-1-yl)-1,2,3,8,9,10-hexahydroanthra[2,1,9-def:6,5,10-d'e'f']diisoquinolin-5-yl)pyrrolidin-2-yl)methyl but-3-enoate (10)

Pyrrolidine-PDI **9** [5-(2-(hydroxymethyl)pyrrolidin-1-yl)-2,9-dioctyl-12-(pyrrolidin-1-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone][18] (30 mg, 0.04 mmol) was dissolved in CH$_2$Cl$_2$ (5 mL). DCC (16 mg, 0.08 mmol), DMAP (2 mg, 0.015 mmol) and 3-butenoic acid (6.5 µL, 0.08 mmol) were added to the solution, and the mixture was stirred at room temperature for 20 h. The solvent was evaporated under reduced pressure. The crude product was dissolved in a few milliliters of EtOAc, the flask was frozen under cold water and filtered through a cotton plug. This procedure was done twice. The product was purified by column chromatography on Silica 60, eluting with CHCl$_3$. Product **10** was obtained as a dark green solid (32 mg, 99%). UV-vis λ_{max}(CHCl$_3$)/nm 272 (ε/dm^3 mol^{-1} cm^{-1} 17040), 434 (11230) and 696 (26120). δ_H(300 MHz; CDCl$_3$; Me$_4$Si): 0.77-0.90 (6H, m, 22-H), 1.15-1.48 (20H, m, 17-21-H), 1.59-1.78 (4H, m, 16-H), 1.88-2.37 (8H, m, c-H, b-H, i-H, j-H), 3.19 (2H, d, *J* 6.2, COCH$_2$), 3.48-3.98 (6H, m, a-H, h-H, k-H), 4.17 (4H, t, *J* 7.3, 15-H), 4.41-4.69 (3H, m, d-H, e-H), 5.07-5.25 (2H, m, CH=C*H*$_2$), 5.80-6.03 (1H, m, C*H*=CH$_2$), 7.44-7.57 (1H, m, 13-H), 8.10 (1H, d, *J* 8.2, 6-*H*), 8.16-8.44 (3H, m, 4-H, 7-H, 14-H), 8.58 (1H, s, 11-H). MS (ESI-TOF, CHCl$_3$/MeOH 10:15): *m/z* = 850.4658 [M]$^+$ (calcd. for C$_{53}$H$_{62}$N$_4$O$_6$ 850.4669).

(1-(2,9-dioctyl-1,3,8,10-tetraoxo-12-(pyrrolidin-1-yl)-1,2,3,8,9,10-hexahydroanthra[2,1,9-def:6,5,10-d'e'f']diisoquinolin-5-yl)pyrrolidin-2-yl)methyl 4-(triethoxysilyl)butanoate (11)

All the glassware was dried in oven (150 °C, 2 h) before use. The reaction flask was sealed with a septum, placed on an ice bath, and kept under constant argon flow. Compound **10** (15 mg, 0.018 mmol) was dissolved in distilled toluene (1 mL) and added to the flask. Triethoxysilane (0.46 mL, 2.5 mmol) and Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Pt ~2%) in xylene; 7.3 µL, 0.88 µmol) were added, and the mixture was stirred in cold under argon. After 10 min, the stirring was continued at room temperature without constant argon flow for 2 h. The crude product was evaporated under reduced pressure using a mechanical vacuum pump. Purification was done on Combiflash chromatograph using alumina column (12 g, purged with argon) eluting with CHCl$_3$/EtOH gradient (flow rate: 30 mL/min; CHCl$_3$ (0.5 min), CHCl$_3$/EtOH 20:1 (2 min)). Product **11** was obtained as a dark green solid (10 mg, 56%). δ_H(300 MHz; CDCl$_3$; Me$_4$Si): 0.51-0.72 (2H, m, COC$_2$H$_4$C*H*$_2$Si), 0.81-0.92 (6H, m, 22-H), 1.12-1.50 (29H, m, 17-21-H, Si(OCH$_2$C*H*$_3$)$_3$), 1.65-1.84 (6H, m, 16-H, COCH$_2$C*H*$_2$CH$_2$Si), 1.86-2.41 (8H, m, c-H, b-H, i-H, j-H), 2.41-2.58 (2H, m, COC*H*$_2$C$_2$H$_4$Si), 3.53-3.96 (12H, m, Si(OC*H*$_2$CH$_3$)$_3$, a-H, h-H, k-H), 4.21 (4H, t, *J* 7.5, 15-H), 4.36-4.77 (3H, m, d-H, e-H), 7.66 (1H, d, *J* 7.9, 13-H), 8.12-8.27 (1H, m, 6-H), 8.31-8.55 (3H, m, 4-H, 7-H, 14-H), 8.59-8.72 (1H, m, 11-H). MS (ESI-TOF, CH$_3$CN): *m/z* = 1014.5597 [M]$^+$ (calcd. for C$_{59}$H$_{78}$N$_4$O$_9$Si 1014.5538).

Complexes

Zn(OTf)$_2$-solution: zinc(II) trifluoromethanesulfonate (36 mg, 0.1 mmol) was dissolved in CHCl$_3$/CH$_3$CN 4:1 (10 mL) by sonication.

Complex Zn-3

Compound **3** (10 mg, 0.009 mmol) was dissolved in CHCl$_3$/CH$_3$CN 4:1 (5 mL) and Zn(OTf)$_2$-solution (0.9 mL, 0.009 mmol) was added. The reaction mixture was stirred at room temperature for 1h. The solvent was evaporated under reduced pressure. Product **Zn-3** was obtained as a dark green solid with quantitative yield (13 mg). UV-vis λ_{max}(CHCl$_3$)/nm 288 (ε/dm^3 mol^{-1} cm^{-1} 49120), 397 (13250), 438 (11950) and 663 (21460). δ_H(300 MHz; CDCl$_3$; Me$_4$Si): 0.76-0.95 (6H, m, 22-H), 1.19-1.51 (20H, m, 17-21-H), 1.63-1.83 (4H, m, 16-*H*), 1.95-2.08 (2H, m, b-H), 2.12-2.38 (2H, m, c-H), 3.41-3.69 (2H, m, a-H), 3.74-4.10 (2H, m, e-H), 4.10-4.33 (4H, m, 15-H), 4.55-4.82 (3H, m, d-H, f-H), 7.28-7.50 (5H, m, g-H), 7.62-7.73 (2H, m, 13-H, phenylene-H), 7.74-7.82 (2H, m, 5″-H), 7.83-7.98 (2H, m, 6-H, phenylene-H), 8.07-8.29 (4H, m, 4″-H, phenylene-H), 8.35-8.49 (2H, m, 7-H, 14-H), 8.51-8.64 (4H, m, 3′-H, 3″-H, 4-H, 11-H), 8.72-8.81 (1H, m, 3″-H), 8.83-8.92 (2H, m, 6″-H), 8.96-9.05 (1H, m, 3′-H). MS (ESI-TOF, CH$_3$CN): *m/z* = 1323.4382 [M-OTf]$^+$ (calcd. for C$_{74}$H$_{70}$F$_3$N$_6$O$_8$SZn 1323.4220).

Complex 3-Zn-3a

Compound **3** (10 mg, 0.009 mmol) was dissolved in CHCl$_3$/CH$_3$CN 4:1 (5 mL) and complex **Zn-3** (13 mg, 0.009 mmol) was added. The reaction mixture was stirred at room temperature for 1h. The solvent was evaporated under reduced pressure. Product **3-Zn-3a** was obtained as a dark green solid with quantitative yield (23 mg). UV-vis λ_{max}(CHCl$_3$)/nm 288 (ε/dm^3 mol^{-1} cm^{-1} 85990), 402 (25290), 439 (23650) and 666 (40230). δ_H(300 MHz; CDCl$_3$; Me$_4$Si): 0.75-0.92 (12H, m, 22-H), 1.17-1.50 (40H, m, 17-21-H), 1.61-1.82 (8H, m, 16-H), 1.91-2.07 (4H, m, b-H), 2.10-2.38 (4H, m, c-H), 3.38-3.67 (4H, m, a-H), 3.72-4.35 (12H, m, 15-H, e-H), 4.53-4.83 (6H, m, d-H, f-H), 7.30-7.51 (14H, m, 5″-H, g-H), 7.54-7.71 (4H, m, 13-H, phenylene-H), 7.77-7.98 (8H, m, 6-H, 6″-H, phenylene-H), 8.00-8.20 (8H, m, 4″-H, phenylene-H), 8.29-8.45 (4H, m, 7-H, 14-H), 8.46-8.64 (4H, m, 4-H, 11-H), 8.71-8.85 (4H, m, 3″-H), 8.94-9.08 (4H, m, 3′-H). MS (ESI-TOF, CH$_3$CN): *m/z* = 2433.9680 [M-OTf]$^+$ (calcd. for C$_{147}$H$_{140}$F$_3$N$_{12}$O$_{13}$SZn 2433.9626).

Complex 3-Zn-3b

Compound **3** (10 mg, 0.009 mmol) was dissolved in CHCl$_3$/CH$_3$CN 4:1 (5 mL) and Zn(OTf)$_2$-solution (0.45 mL, 0.0045 mmol) was added. The reaction mixture was stirred at room temperature for 1h. The solvent was evaporated under reduced pressure. Product **3-Zn-3b** was obtained as a dark green solid with quantitative yield (12 mg). UV-vis $\lambda_{max}(CHCl_3)$/nm 288 (ε/dm^3 mol^{-1} cm^{-1} 89130), 403 (26730), 442 (24770) and 666 (41100). δ_H(300 MHz; $CDCl_3$; Me_4Si): 0.77-0.90 (12H, m, 22-H), 1.16-1.50 (40H, m, 17-21-H), 1.62-1.83 (8H, m, 16-H), 1.94-2.08 (4H, m, b-H), 2.11-2.39 (4H, m, c-H), 3.40-3.68 (4H, m, a-H), 3.73-4.30 (12H, m, 15-H, e-H), 4.54-4.80 (6H, m, d-H, f-H), 7.28-7.51 (14H, m, 5″-H, g-H), 7.58-7.73 (4H, m, 13-H, phenylene-H), 7.79-8.00 (8H, m, 6-H, 6″-H, phenylene-H), 8.01-8.24 (8H, m, 4″-H, phenylene-H), 8.33-8.46 (4H, m, 7-H, 14-H), 8.50-8.64 (4H, m, 4-H, 11-H), 8.72-8.83 (4H, m, 3″-H), 8.96-9.07 (4H, m, 3′-H),. MS (ESI-TOF, CH_3CN): *m/z* = 2433.9766 [M-OTf]$^+$ (calcd. for $C_{147}H_{140}F_3N_{12}O_{13}SZn$ 2433.9626).

Complex Zn-8

Compound **8** (10 mg, 0.008 mmol) was dissolved in $CHCl_3/CH_3CN$ 4:1 (5 mL) and $Zn(OTf)_2$-solution (1.6 mL, 0.016 mmol) was added. The reaction mixture was stirred at room temperature for 1h. The solvent was evaporated under reduced pressure. Product **Zn-8** was obtained as a dark red solid with quantitative yield (16 mg). UV-vis $\lambda_{max}(CHCl_3)$/nm 288 (ε/dm^3 mol^{-1} cm^{-1} 47680), 338 (28780) and 553 (13980). δ_H(300 MHz; $CDCl_3$; Me_4Si): 0.84-0.92 (6H, m, 22-H), 1.25-1.48 (20H, m, 17-21-H), 1.70-1.88 (4H, m, 16-H), 3.97-4.36 (4H, m, 15-H), 7.70-7.89 (5H, m, phenylene-H), 7.92-8.03 (5H, m, 5″-H, phenylene-H), 8.18-8.49 (12H, m, 4″-H, 4-H, 6-H, 7-H, 11-H, 13-H, 14-H, phenylene-H), 8.88-9.02 (8H, m, 3″-H, 6″-H), 9.11 (4H, s, 3′-H). MS (ESI-TOF, CH_3CN): *m/z* = 1803.2660 [M-OTf]$^+$ (calcd. for $C_{85}H_{68}F_9N_8O_{13}S_3Zn_2$ 1803.2507).

Complex 3-Zn-8

Complex **Zn-8** (16 mg, 0.008 mmol) and compound **3** (20 mg, 0.018 mmol) were dissolved in DMF (7 mL). The reaction mixture was stirred at room temperature for 2h. The solvent was evaporated under reduced pressure using a mechanical vacuum pump. Product **3-Zn-8** was obtained as a dark green solid with quantitative yield (34 mg). UV-vis $\lambda_{max}(CHCl_3)$/nm 288 (ε/dm^3 mol^{-1} cm^{-1} 118050), 389 (42710), 439 (31690) and 666 (48620). δ_H(300 MHz; $CDCl_3$; Me_4Si): 0.76-0.95 (18H, m, 22-H), 1.15-1.52 (60H, m, 17-21-H), 1.62-1.83 (12H, m, 16-H), 1.93-2.08 (4H, m, b-H), 2.13-2.30 (4H, m, c-H), 3.41-3.68 (4H, m, a-H), 3.76-4.37 (16H, m, 15-H, e-H), 4.55-4.86 (6H, m, d-H, f-H), 7.29-7.51 (17H, m), 7.54-7.80 (11H, m), 7.82-8.00 (11H, m), 8.02-8.28 (15H, m), 8.31-8.67 (15H, m), 8.70-8.94 (9H, m), 8.96-9.27 (6H, m). MS (ESI-TOF, CH_3CN): *m/z* = 1937.6973 [M-2(OTf)]$^{2+}$ (calcd. for $C_{230}H_{206}F_6N_{20}O_{20}S_2Zn_2$ 1937.6901).

Immobilization and complexation

Quartz plates were cleaned according to the process reported earlier.[4] The reaction vessel was cooled down after being in oven (2h, 150 °C). Siloxane compound (**6**, **11**) (2 mg) was dissolved in distilled toluene (20 mL) and loaded in the reaction vessel under argon. Isopropyl amine (0.4 mL) was added and the cleaned plates were immersed in the solution. The reaction vessel was filled with argon and heated at 105 °C for 2h. After an appropriate time the plates were sonicated twice in toluene and once in CH_2Cl_2, 15 s in each solvent, and the samples were dried in argon flow (30 min).

Complexation of the SAM of tpy-PDI **6** was done by immersing the samples into solutions of the corresponding metal ions. *Zn-solution:* zinc(II) trifluoromethanesulfonate (36 mg, 0.1 mmol) was dissolved in $CHCl_3/CH_3CN$ 4:1 (10 mL) by sonication. For complexation the stock solution (3.6 mL) was diluted with $CHCl_3/CH_3CN$ 4:1 (20 mL). The plates with SAMs were immersed in the salt solution and kept there for 1h. After an appropriate time, the plates were washed with $CHCl_3/CH_3CN$ 4:1, and the samples were dried in argon flow.

Conclusions

We have synthesized PDIs with terpyridine groups and silane anchors at the *bay*-region. Both of these groups are rarely found in this position of PDIs. Supramolecular dimer and trimer structures were constructed from the monomers via the terpyridine moieties and zinc ions. A trimer complex showed efficient energy transfer from the middle PDI to the side PDIs. The silane-containing PDIs were attached on the quartz substrate and coordination of zinc was also done on the surface. Formation of the complex was observed clearly in steady-state absorption measurements. The molecular films were not obtained as perfect monolayers, but demonstrate the potential to construct supramolecular assemblies of PDI directly on a solid substrate. This implies that attention should be paid on the surface-PDI tether, and these studies are currently under way.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Fluorescence decays of PDI **8** and PDI **3**. ^{1}H NMR, ^{13}C NMR and gHSQC NMR spectra of compounds **1**, **3-6**, **8**, **10** and **11**. ^{1}H NMR spectra of complexes **Zn-3**, **Zn-8**, **3-Zn-3a**, **3-Zn-3b** and **3-Zn-8**. Mass spectra of complexes **3-Zn-3b** and **3-Zn-8**. See DOI: 10.1039/b000000x/

1 A. Ulman, *Chem. Rev.*, 1996, **96**, 1533; E. Sariola, A. Kotiaho, N. V. Tkachenko, H. Lemmetyinen and A. Efimov, *J. Porphyrins Phthalocyanines*, 2010, **14**, 397.

2 J. Sagiv, *J. Am. Chem. Soc.*, 1980, **102**, 92; Y. Yang, A. M. Bittner, S. Baldelli and K. Kern, *Thin Solid Films*, 2008, **516**, 3948.

3 C. Baik, D. Kim, M-S. Kang, S. O. Kang, J. Ko, M. K. Nazeeruddin and M. Grätzel, *J. Photochem. Photobiol., A*, 2009, **201**, 168.

4 E. Sariola-Leikas, M. Hietala, A. Veselov, O. Okhotnikov, S. L. Semjonov, N. V. Tkachenko, H. Lemmetyinen and A. Efimov, *J. Colloid Interface Sci.*, 2012, **369**, 58.

5 M. Chiper, R. Hoogenboom and U. S. Schubert, *Macromol. Rapid Commun.*, 2009, **30**, 565; A. Winter, S. Hoeppener, G. R. Newkome and U. S. Schubert, *Adv. Mater.*, 2011, **23**, 3484.

6 Y-Y. Chen, Y-T. Tao and H-C. Lin, *Macromolecules*, 2006, **39**, 8559.

7 A. R. Rabindranath, A. Maier, M. Schäfer and B. Tieke, *Macromol. Chem. Phys.*, 2009, **210**, 659.

8 T-Y. Dong, M-C. Lin, M. Y-N. Chiang and J-Y. Wu, *Organometallics*, 2004, **23**, 3921; H. Wolpher, S. Sinha, J. Pan, A. Johansson, M. J. Lundqvist, P. Persson, R. Lomoth, J. Bergquist, L. Sun, V. Sundström, B. Åkermark and T. Polívka, *Inorg. Chem.*, 2007, **46**, 638.

View Article Online
DOI: 10.1039/C3OB41058G

9 H. Hofmeier, J. Pahnke, C. H. Weidl and U. S. Schubert, *Biomacromolecules*, 2004, **5**, 2055; P. D. Vellis, J. A. Mikroyannidis, C-N. Lo and C-S. Hsu, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 7702; K. W. Cheng, C. S. C. Mak, W. K. Chan, A. M. C. Ng and A. B. Djurišić, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 1305.

10 F. Würthner, *Chem. Commun.*, 2004, 1564; C. Huang, S. Barlow and S. R. Marder, *J. Org. Chem.*, 2011, **76**, 2386.

11 F. Würthner, V. Stepanenko, Z. Chen, C. R. Saha-Möller, N. Kocher and D. Stalke, *J. Org. Chem.*, 2004, **69**, 7933.

12 D. Wang, Y. Shi, C. Zhao, B. Liang and X. Li, *J. Mol. Struct.*, 2009, **938**, 245; M. Queste, C. Cadiou, B. Pagoaga, L. Giraudet and N. Hoffmann, *New J. Chem.*, 2010, **34**, 2537; V. L. Gunderson, E. Krieg, M. T. Vagnini, M. A. Iron, B. Rybtchinski and M. R. Wasielewski, *J. Phys. Chem. B*, 2011, **115**, 7533; S. Dey, A. Efimov and H. Lemmetyinen, *Eur. J. Org. Chem.*, 2012, 2367.

13 R. Dobrawa, M. Lysetska, P. Ballester, M. Grüne and F. Würthner, *Macromolecules*, 2005, **38**, 1315.

14 V. Stepanenko, M. Stocker, P. Müller, M. Büchner and F. Würthner, *J. Mater. Chem.*, 2009, **19**, 6816; M. T. Rawls, J. Johnson and B. A. Gregg, *J. Electroanal. Chem.*, 2010, **650**, 10.

15 G. Golubkov, H. Weissman, E. Shirman, S. G. Wolf, I. Pinkas and B. Rybtchinski, *Angew. Chem. Int. Ed.*, 2009, **48**, 926.

16 T. van der Boom, G. Evmenenko, P. Dutta and M. R. Wasielewski, *Chem. Mater.*, 2003, **15**, 4068; N. Mizoshita, T. Tani and S. Inagaki, *Adv. Funct. Mater.*, 2011, **21**, 3291; H. Rathnayake, J. Binion, A. McKee, D. J. Scardino and N. I. Hammer, *Nanoscale*, 2012, **4**, 4631; N. Mizoshita, T. Tani and S. Inagaki, *Adv. Mater.*, 2012, **24**, 3350.

17 N. Tuccitto, I. Delfanti, V. Torrisi, F. Scandola, C. Chiorboli, V. Stepanenko, F. Würthner and A. Licciardello, *Phys. Chem. Chem. Phys.*, 2009, **11**, 4033; M. L. Hassan, C. M. Moorefield, H. S. Elbatal, G. R. Newkome, D. A. Modarelli and N. C. Romano, *Mater. Sci. Eng., B*, 2012, **177**, 350.

18 R. K. Dubey, M. Niemi, K. Kaunisto, A. Efimov, N. V. Tkachenko and H. Lemmetyinen, *Chem. Eur. J.*, DOI: 10.1002/chem.201203387.

19 R. K. Dubey, A. Efimov and H. Lemmetyinen, *Chem. Mater.*, 2011, **23**, 778.

20 A. L. Bramblett, M. S. Boeckl, K. D. Hauch, B. D. Ratner, T. Sasaki and J. W. Rogers Jr., *Surf. Interface Anal.*, 2002, **33**, 506.

21 M. Vrábel, M. Hocek, L. Havran, M. Fojta, I. Votruba, B. Klepetářová, R. Pohl, L. Rulíšek, L. Zendlová, P. Hobza, I-H. Shih, E. Mabery and R. Mackman, *Eur. J. Org. Chem.*, 2007, 1752.