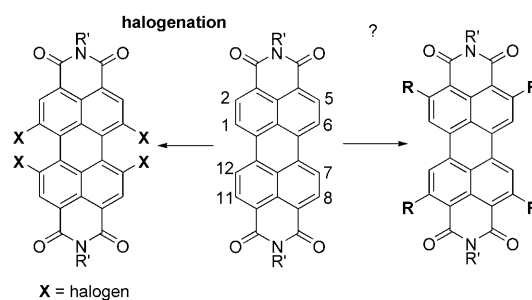


Regioselective Ru-Catalyzed Direct 2,5,8,11-Alkylation of Perylene Bisimides

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Perylene tetracarboxylic acid bisimides (PBIs) are an important class of dyes and pigments for widespread practical use, which have been extensively investigated for a long time both in academia and industry.^[1] Recently, they have also received much attention as n-type semiconducting materials.^[2] Furthermore, owing to high fluorescence quantum efficiency and photostability, they have been a popular motif for single-molecule spectroscopy.^[3] Chemical modifications of PBIs are quite important to gain desirable photo-physical and electronic properties as well as solubility. In spite of their rich material chemistry, functionalization of the perylene core of PBIs relies on halogenation of the bay area (1,6,7,12-positions) and subsequent transformations (Scheme 1).^[4] Selective functionalization at 2,5,8,11-positions remains unavailable to date.^[5]

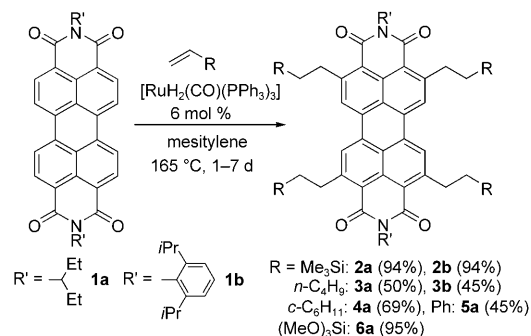
Here we wish to disclose the first selective synthesis of 2,5,8,11-substituted PBIs. We have envisioned the potential



Scheme 1. Functionalization of perylene bisimides.

of direct functionalization of PBIs by organometallic and catalytic means: ruthenium-catalyzed C–H bond activation and addition strategy, namely, the Murai–Chatani–Kakiuchi protocol (Scheme 2).^[6] This reaction can introduce alkyl substituents to the proximal position of the directing groups. Successful installation of alkyl chains at the 2,5,8,11-positions of PBIs would allow greater modification of properties in the solid state or condensed phase.

The reaction procedure is quite simple. A mixture of bis(*N*-ethylpropyl)PBI **1a** and trimethylvinylsilane was heated in mesitylene at 165 °C for 60 h in the presence of



Scheme 2. Ru-catalyzed selective alkylation of perylene bisimides.

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6 mol% of $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$. After silica-gel separation, tetraalkylated PBI 2a was obtained in 94% yield (Scheme 2). The alkylation of *N*-(2,6-diisopropyl)phenylPBI 1b needed longer reaction times due to its lower solubility, but afforded the desired product 2b in almost quantitative yield. After tetraalkylation, solubility in organic solvents is significantly enhanced: 2a is soluble in ethyl acetate and 3a is soluble in warm hexane. A particularly attractive feature is facile introduction of the alkoxyisilyl side chain (6a) that serves as a docking group for inorganic substrates (see below).

UV/Vis absorption and fluorescence spectra are shown in Figure 1. As expected, the alkylation does not significantly change the absorption and emission properties in the solution state, but somewhat lowers molar extinction coefficients of the lowest energy absorption band. Fluorescence quantum yields in toluene are almost the same as the parent PBIs 1a and 1b. Importantly, alkylated PBIs fluoresce even in the solid state with intense red emission.^[7] For example, a powder sample of 3a emits at 635 nm with a much enhanced quantum yield of 0.59 (Table 1). The fluorescence spectra in the solid state are broad and substantially red-shifted, suggesting emission from aggregates of PBI. In sharp contrast to the solution state, quantum yields in the solid state heavily depend on the introduced alkyl groups, implying the importance of alkyl substituents that influence the crystal packing. Absorption spectra in the solid state were measured for microdispersion of PBIs (Figure 1c).^[8] PBI 1a exhibits a broad and blue-shifted spectrum, which is typical for H-type aggregates. For 3a and 4a, the absorption features in solution including the vibronic bands were preserved in the solid state, but 3a showed 12 nm of red-shift. These results indicate smaller intermolecular electronic interaction in crystal than parent PBI 1a by the introduced alkyl substituents.

The structure of PBI 4a has been clearly elucidated by the X-ray analysis (Figure 2 and Figure S31).^[9] Introduction of four alkyl groups does not result in any distortion of the flat perylene core. This is in sharp contrast to bay-area substitution, which often induces severe twist in perylene. Each molecule of 4a aligns in a parallel manner without stacking. Obviously, the interaction between alkyl groups is essential to form this type of aggregation. In contrast, PBI 2a exhibits the herringbone arrangement with distinct π -stacking of an interplanar distance of about 3.6 Å.^[10] Two molecules are crossed with each other by 66°, resulting from steric hindrance of bulky silylethyl substituents. Although it was difficult to obtain a nice single crystal of 3a, the synchrotron powder X-ray diffraction (SXRD) revealed a high crystallinity of 3a with the triclinic symmetry.

Table 1. Photophysical properties of alkylated PBIs.

PBI	ϵ [$\text{M}^{-1}\text{cm}^{-1}$]	λ_{max} [nm] ^[a]	λ_{em} [nm] ^[b]	Stokes shift [cm ⁻¹]	F_f (solution)	λ_{em} [nm] (solid)	F_f (solid) ^[c]
1a	$8.43 \cdot 10^4$	526	533	250	1.0	676	0.07
2a	$5.97 \cdot 10^4$	522	533	414	0.91	640	0.41
3a	$6.42 \cdot 10^4$	521	533	380	0.94	635	0.59
4a	$5.30 \cdot 10^4$	521	533	451	0.95	644	0.24
5a	$5.19 \cdot 10^4$	525	534	339	0.92	634	0.08
1b	$8.50 \cdot 10^4$	527	534	249	0.97	–	0.01
2b	$6.29 \cdot 10^4$	524	534	357	0.94	584	0.02
3b	$6.80 \cdot 10^4$	523	533	358	0.94	591	0.09

[a] The longest absorption maxima. [b] Excited at the longest absorption maxima. [c] Excited at 470 nm. Absolute quantum yields were determined by a calibrated integrating sphere system within 3% errors. Powder samples were prepared by recrystallization of alkylated PBIs from $\text{CHCl}_3/\text{CH}_3\text{CN}$.

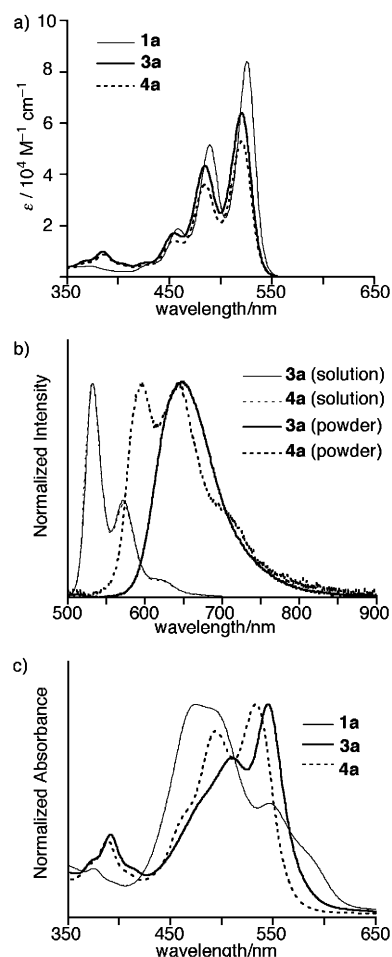


Figure 1. a) UV/vis absorption spectra in toluene. b) Emission spectra in toluene and solid state emission spectra. c) Solid-state absorption spectra of dispersion of PBIs in water.

Using trimethoxysilyl groups, 6a can be chemisorbed on a glass surface via the following process: 1) recovery of the OH groups on the glass surface, 2) dropping a toluene solution of 6a on the surface; 3) removal of the physisorbed PBI. We were able to obtain a fluorescence image of single molecules of 6a adsorbed on glass surface. The fluorescence is still observable, even though the molecule is exposed to

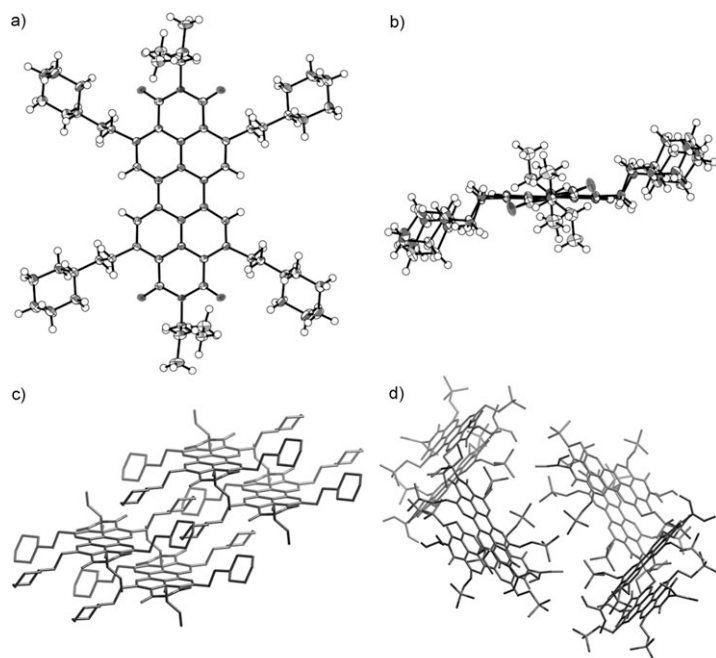


Figure 2. X-ray structure of 4a. a) Top view and b) side view. The thermal ellipsoids are at the 50% probability level. Crystal packing of c) 4a and d) 2a.

air and not in the polymer (PMMA) matrix where the single molecules can be dispersed, immobilized, and fluoresce. We measured the fluorescence intensity trajectories (FITs) of single molecules both on glass surface and in the polymer matrix. While one-step and stable FITs are observed in the polymer matrix, the representative FIT of 6a on glass surface shows fluorescence intensity fluctuation with off-states

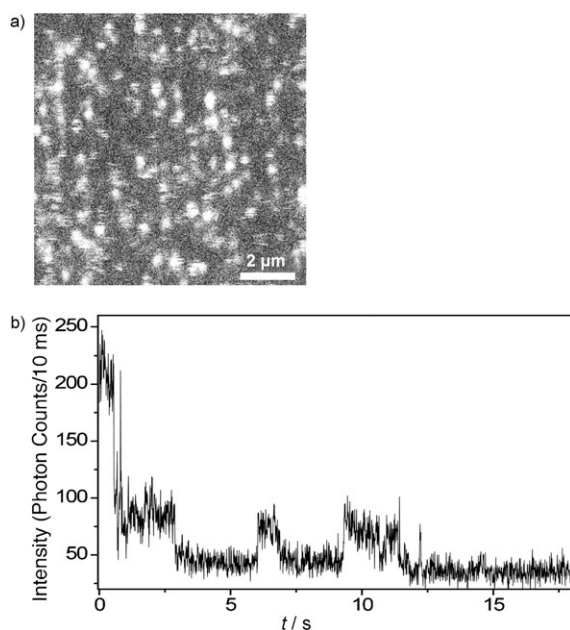


Figure 3. a) Fluorescence image and b) fluorescence intensity trajectory of 6a on glass surface.

of a few seconds that is probably induced by interaction between PBI and covalent-bonded glass substrate, such as electron transfer to the impurity sites in the glass (Figure 3 and Figure S34).^[11]

In conclusion, we have developed a direct introduction of alkyl groups to 2,5,8,11-positions of perylene bisimides on the basis of ruthenium-catalyzed C–H bond activation. Such alkylations have a significant influence on the solid-state properties as exemplified by the intense red emission. The usefulness of this protocol has been demonstrated by preliminary single-molecule spectroscopy of 6a on glass surface, which was facilitated through facile introduction of alkoxy-silyl groups to PBI. Thus, we can study the inherent optical properties of single molecules without any hindrance from the surrounding polymer matrix. This direct protocol represents a promising perspective for a chelation-assisted strategy for the selective functionalization of PBIs at 2,5,8,11-positions.

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Keywords: alkylation · fluorescence · perylenes · ruthenium · single-molecule studies

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- [9] Crystal data for 4a: $C_{66}H_{86}N_2O_4$, $M_w=971.37$, triclinic, space group $P\bar{1}$ (No. 2), $a=6.299(3)$, $b=10.967(6)$, $c=19.506(9)$, $\alpha=78.896(19)$, $\beta=85.019(19)$, $\gamma=84.60(2)^\circ$, $V=1313.2(11)$ Å³, $Z=1$, $I_{\text{calcd}}=1.228$ g cm⁻³, $T=123(2)$ K, 12876 measured reflections, 5966 unique reflections, $R=0.0587$ ($I > 2.0\sigma(I)$), $R_w=0.1800$ (all data), $GOF=1.086$ ($I > 2.0\sigma(I)$).
- [10] Preliminary crystal data for 2a: $C_{34}H_{77}N_2O_4Si_4$, $M_w=930.54$, orthorhombic, space group $Pca n$ (No. 60), $a=9.905(4)$, $b=30.784(12)$, $c=35.381(14)$ Å, $V=10789(7)$ Å³, $Z=8$, $I_{\text{calcd}}=1.146$ g cm⁻³, $T=90(2)$ K, 46252 measured reflections, 8468 unique reflections, $R=0.1803$ ($I > 2.0\sigma(I)$), $R_w=0.4670$ (all data), $GOF=1.187$ ($I > 2.0\sigma(I)$). 2a also afforded single crystals from dioxane with different packing (SI). CCDC 726128 (4a), 726126 (2a), and 726127 (2a from dioxane) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif
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