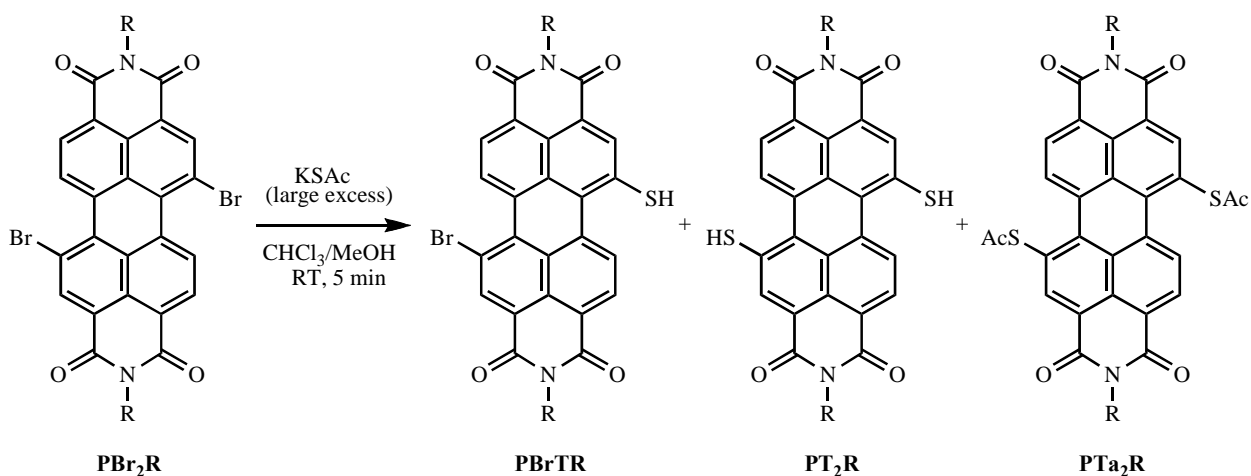


## Supplementary Information for Bis-Dithiano Perylene Diimide: Synthesis and Characterization of a Novel Ring System

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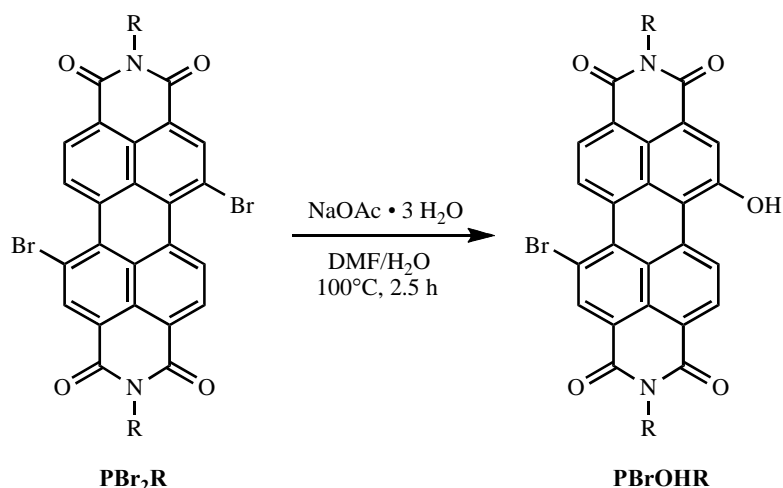
Our findings demonstrate that bromo substituents at the bay positions of perylene diimides are readily displaced under very mild conditions by potassium thioacetate resulting in the subject dithiane annulations. Moreover, reaction of bromo perylene diimides with sodium acetate was found to produce hydroxy substitution (Scheme S2). Tentative structures for some of the isolated intermediate products in the annulation transformations have been presented earlier (Schemes 2 and 3). An additional intermediate, obtained under somewhat different reaction conditions, is presented in Scheme S1. The supplementary information below also includes reaction schemes (S3 and S4), experimental details and spectral data relating to preparation of the bromo-substituted precursors of the new sulfur-annulated subject compounds.

In addition to the two isolated intermediate products presented in Scheme 1 (right), another intermediate product was isolated when **PBr<sub>2</sub>R** was reacted with potassium thioacetate under different conditions. Instead of using a small stoichiometric excess of potassium thioacetate, the different interception experiment involved a large excess of potassium thioacetate for only a short reaction time (5 min). Under these conditions, TLC analysis indicated that the starting dibromo compounds **PBr<sub>2</sub>R** were rapidly and completely converted to a difficultly separable mixture. The NMR spectrum of the impure isolated intermediate products suggested a mixture that was mostly composed of approximately equal amounts of the same two tentative structures **PBrTR** and **PT<sub>2</sub>R**. In addition, there was also isolated a very small amount of another transient product, which was tentatively identified as di-thioacetyl derivative **PTa<sub>2</sub>R**. Further treatment of these intercepted compounds with excess potassium thioacetate yielded a product mixture that was composed mainly of the two annulated products **PS<sub>4</sub>** and **PS<sub>3</sub>**, as described previously.



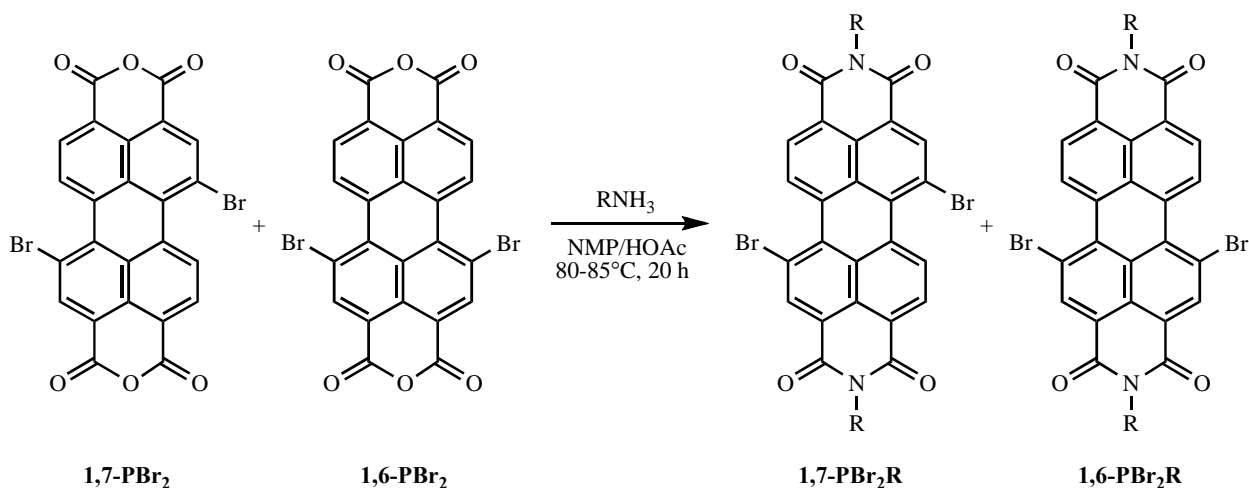
**Scheme S1.** Formation of intermediate products from **PBr<sub>2</sub>R**.

Related to the displacement of the bromo substituents of **PBr<sub>2</sub>R** with potassium thioacetate, we observed that reaction of **PBr<sub>2</sub>R** with a large excess of sodium acetate hydrate in DMF at 100°C afforded cleanly an 83% isolated yield of a single red-purple product identified as **PBrOHR** (Scheme S2). Efforts to force displacement of the second bromine atom using higher temperatures or potassium hydroxide only resulted in intractable product mixtures. Although **PBr<sub>2</sub>R** was actually determined by NMR to be an approximately 85:15 mixture of 1,7- and 1,6-isomers, respectively, no NMR signals were in evidence to clearly indicate that **PBrOHR** was a mixture of positional isomers, which would be expected to be difficultly resolvable. Other researchers<sup>1</sup> have reported a substituted perylene diimide similar to **PBrOHR** as the product of reaction of a corresponding dibromo derivative with N-methylpiperazine in NMP containing a trace of water.



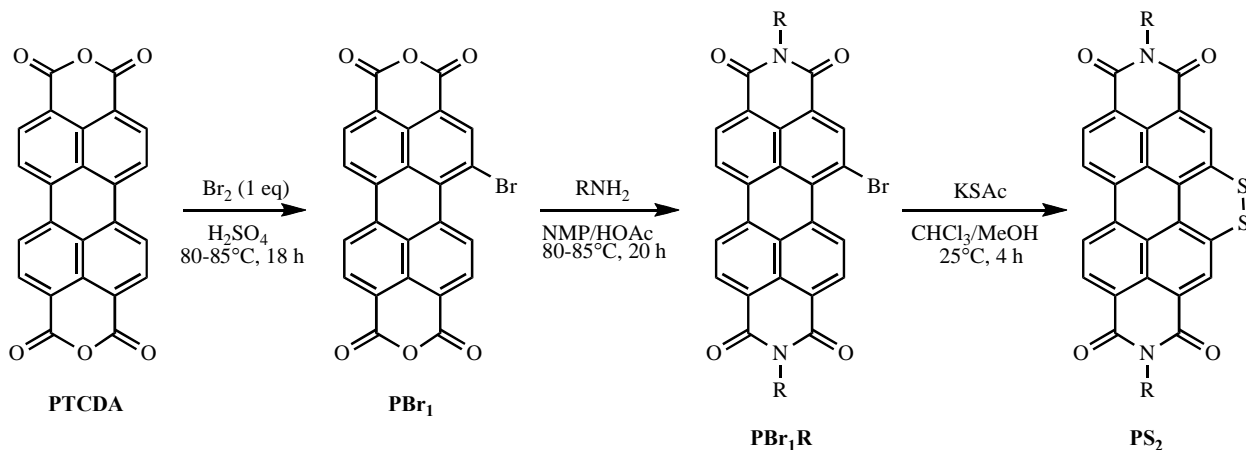
**Scheme S2.** Reaction of **PBr<sub>2</sub>R** with sodium acetate.

As presented in Scheme S3, dibromo-diimide **PBr<sub>2</sub>R** (as a mixture of 1,7- and 1,6-isomers) was prepared in 66% isolated yield by condensation of known dibromo-dianhydride **PBr<sub>2</sub>** (as a mixture of 1,7- and 1,6-isomers) with amine **RNH<sub>2</sub>**. The latter amine was readily available in 84% overall yield employing our previously reported procedures.<sup>2</sup> Dibromo-diimide **PBr<sub>2</sub>R** was obtained as an approximately 85:15 inseparable mixture of 1,7- and 1,6-isomers, respectively (NMR estimate). The procedure for preparation of the dibromo-perylene dianhydrides **PBr<sub>2</sub>** was adapted from that reported by Würthner, *et al.*<sup>3</sup> Our modified procedure employed a small excess of bromine in commercial concentrated (rather than 100%) sulfuric acid at the cooler reaction temperature of 60°C. Thus, we obtained a 96% yield of **PBr<sub>2</sub>** as an approximately 85:15 inseparable mixture of 1,7- and 1,6-isomers, respectively. The quality and composition of the bromination product was conveniently ascertained by NMR analysis of the corresponding soluble potassium tetracarboxylate, which was obtained by heating the product dianhydride sample with potassium carbonate in D<sub>2</sub>O.



**Scheme S3.** Preparation of **PBr<sub>2</sub>R**.

The preparation of mono-dithiano perylene diimide **PS<sub>2</sub>** was similar to that of bis-dithiano perylene diimide **PS<sub>4</sub>**, which was presented in Scheme 1. Thus, **PS<sub>2</sub>** was obtained in 73% isolated yield from monobromo diimide **PBr<sub>1</sub>R**, as described earlier. The complete preparation of **PS<sub>2</sub>** beginning with known monobromo anhydride **PBr<sub>1</sub>**<sup>4</sup> is outlined in Scheme S4. Langhals and Kirner<sup>5</sup> reported formation of an analogous dithiano structure by heating at about 130°C a mononitro precursor with sulfur in DMF solution. The spectral characteristics of **PS<sub>2</sub>** were comparable to those reported for this analogous dithiano compound.



**Scheme S4.** Preparation of **PS<sub>2</sub>**.

Our most successful, albeit still disappointing, preparation of starting material **PBr<sub>1</sub>** derived from procedures described by Wang, *et al.*<sup>4</sup> NMR analysis (D<sub>2</sub>O/K<sub>2</sub>CO<sub>3</sub>) of the product thus obtained indicated an approximately 1:2:3 ratio of **PTCDA**, **PBr<sub>1</sub>** and **PBr<sub>2</sub>**, respectively. Because of the insolubility of these anhydrides, the unpurified mixture was converted directly to the corresponding diimides. Pure **PBr<sub>1</sub>R** was then isolated by chromatography.

Other approaches to improve our synthetic preparation of **PBr<sub>1</sub>R** were unsuccessful because of disappointing efforts to brominate the perylene core. For example, reaction of our previously described **PPEEB**<sup>2</sup> with bromine/potassium carbonate, as described by Langhals and Kirner,<sup>5</sup> afforded an impure product whose NMR spectrum indicated no reaction at the perylene core but rather an uncharacterized apparent modification of the polyoxyethylene chain. Similarly, attempted monobromination of **PPEEB** according to procedures of Rybtchinski, *et al.*,<sup>6</sup> also yielded products that appeared to result from reaction not at the perylene core but rather at the polyoxyethylene chain. No further efforts were made to investigate these reactions or the products therefrom.

### Supporting Information Experimental Section

**PTa<sub>2</sub>R.** A solution of 250 mg (2.2 mmol) of potassium thioacetate in 10 mL of methanol was added at once to a solution of 100 mg (0.11 mmol) of **PBr<sub>2</sub>R** in 10 mL of chloroform. After stirring at room temperature for 5 min, the reaction was quenched by addition of 1 mL of glacial acetic acid. TLC analysis indicated complete consumption of the starting material. Usual workup and silica gel chromatography (2% methanol in methylene chloride eluent) yielded 70 mg (74%) of a product mixture composed of approximately equal amounts of mainly **PT<sub>2</sub>R** and **PTBrR**. In addition, a 2-mg impure sample (3%) of a more mobile product was isolated and tentatively identified as **PTa<sub>2</sub>R**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.89 (t, *J* = 7.4 Hz, 6 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.34 (br sextet, *J* = 7.2 Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.54 (br quintet, *J* = 7.6 Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.06 (quintet, *J* = 7.0 Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.48 (s, 6 H, CO-CH<sub>3</sub>), 3.44 (t, *J* = 6.6 Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>),

3.52-3.65 (m, 20 H, OCH<sub>2</sub>), 4.32 (br t, *J* = 6.6 Hz, 4 H, NCH<sub>2</sub>), 8.69 (d, 2 H, *J* = 8.4 Hz, Ar-*H*), 8.72 (s, 2 H, Ar-*H*), 8.82 (d, 2 H, *J* = 8.0 Hz, Ar-*H*).

**PBrOHR.** A reaction mixture composed of 0.40 g (0.42 mmol) of **PBr<sub>2</sub>R** and 1.00 g (7.4 mmol) of sodium acetate trihydrate in 40 mL of DMF was heated in a bath at about 100°C for 2 h. An 80-ml portion of water was added, and heating was continued at 100°C for 30 m. An additional 100 mL of water was added, followed by 2 mL of concentrated hydrochloric acid. The crude product was isolated by filtration and purified by silica gel chromatography (5% methanol in methylene chloride eluent) to yield 0.31 g (83%) of a red-purple solid: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.81 and 0.89 (t, *J* = 7.2 Hz, 6 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.24-1.38 (m, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.47-1.61 (m, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.99 and 2.08 (br quintet, *J* = 6.8 Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.42 and 3.43 (t, *J* = 6.8 Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.60-3.73 (m, 20 H, OCH<sub>2</sub>), 4.15 and 4.30 (br t, *J* = 7.2 Hz, 4 H, NCH<sub>2</sub>), 8.33 (s, 1 H, Ar-*H*), 8.44 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 8.50 (s, 1 H, Ar-*H*), 8.51 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 9.39 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 9.46 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 9.68 (br, 1 H, OH). MS (MALDI-TOF): found, 888.2, 890.2; calcd for C<sub>46</sub>H<sub>53</sub>BrN<sub>2</sub>O<sub>11</sub>, 889.84. The observed multiple NMR signals for the polyoxyethylene chain, as well as six aromatic signals, are consistent with the structure of a perylene diimide that is unsymmetrically disubstituted at the bay positions. Signals for the expected isomeric 1,6-isomer were not evident although they would be expected to be difficult to resolve.

**1,7(6)-dibromoperylene-3,4,9,10-tetracarboxylic dianhydride (PBr<sub>2</sub>).** A mixture of 5.00 g (12.8 mmol) of **PTCDA** in 125 mL of concentrated sulfuric acid was stirred overnight at room temperature. The reaction mixture was then placed in a bath at 60°C, and a 150-mg (0.6 mmol) portion of iodine was added. A 2-mL (6.2 g, 39 mmol) portion of bromine was added at once, and the reaction mixture was stirred at 60°C. After 46 h, analysis by NMR (D<sub>2</sub>O/K<sub>2</sub>CO<sub>3</sub>) indicated that all of the **PTCDA** starting material as well as the competitively formed monobromo derivative **PBr<sub>1</sub>** had been completely consumed. The reaction mixture was then cooled to room temperature, and the excess of bromine was removed in a stream of nitrogen. The reaction mixture was carefully added to 250 g of ice. The resulting precipitate was collected by filtration using a fine frit glass

funnel. Several washings with large amounts of water followed by oven-drying at 90°C afforded 6.70 g (96%) of red powder that was not purified further.

Conversion of a sample of this product to the corresponding soluble potassium tetracarboxylate provided a convenient means of analysis. Thus, a sample of the crude product was dissolved by heating in D<sub>2</sub>O containing K<sub>2</sub>CO<sub>3</sub>. The major isomer **1,7-PBr<sub>2</sub>** exhibited the following spectrum: <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O/K<sub>2</sub>CO<sub>3</sub>): δ 7.69 (d, *J* = 7.6 Hz, 2 H), 7.91 (s, 2 H), 8.78 (d, *J* = 7.6 Hz, 2 H). The following signals were observed for the minor isomer **1,6-PBr<sub>2</sub>**: <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O/K<sub>2</sub>CO<sub>3</sub>): δ 7.70 (d, *J* = 7.6 Hz, 2 H), 7.93 (s, 2 H), 8.81 (d, *J* = 7.6 Hz, 2 H). Analysis of the NMR spectrum indicated an approximately 85:15 mixture, respectively, of the two isomeric dibromo dianhydrides. No other signals were observed in two preparations. In two other preparations, small amounts (<4%) of unreacted **PTCDA** were detected.

**1-bromoperylene-3,4,9,10-tetracarboxylic dianhydride (PBr<sub>1</sub>)**. Procedures described by Wang, *et al.*<sup>4</sup> were used to prepare **PBr<sub>1</sub>**. NMR analysis (D<sub>2</sub>O/K<sub>2</sub>CO<sub>3</sub>) of the isolated product indicated an approximately 1:2:3 ratio of **PTCDA**, **PBr<sub>1</sub>** and **PBr<sub>2</sub>**, respectively. No attempt was made to separate these compounds. As was done above for **PBr<sub>2</sub>**, NMR analysis of this product was accomplished by dissolving a sample in D<sub>2</sub>O containing K<sub>2</sub>CO<sub>3</sub>. The following signals in the NMR spectrum were attributed to **PBr<sub>1</sub>**: <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O/K<sub>2</sub>CO<sub>3</sub>): δ 7.65-7.69 (m, 3 H), 7.90 (s, 1 H), 8.18 (br d, *J* = 7.6 Hz, 2 H), 8.94 (d, *J* = 7.6 Hz, 1 H). The following signals in the NMR spectrum were attributed to **PTCDA**: <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O/K<sub>2</sub>CO<sub>3</sub>): δ 7.63 (d, *J* = 8.0 Hz, 4 H), 8.24 (d, *J* = 8.0 Hz, 4 H).

**1,7(6)-Dibromo-*N,N'*-bis[3-[2-[2-(butoxy)ethoxy]ethoxy]propyl]perylene-3,4,9,10-tetracarboxyldiimide (PBr<sub>2</sub>R)**. A reaction mixture composed of 1.31-g (6.0 mmol) of **RNH<sub>2</sub>**, 1.10 g (2.0 mmol) of **PBr<sub>2</sub>** (containing about 15% of **1,6-PBr<sub>2</sub>**) and 0.7 mL (12 mmol) of glacial acetic acid in 15 mL of NMP under a nitrogen atmosphere was heated in a bath at 80-85°C for 20 h. The resulting mixture was diluted with 150 mL of water, and the crude product was isolated by suction filtration. Column chromatography on silica gel (5% methanol in methylene chloride eluent) yielded 1.25 g (66%) of a waxy red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.89 (t, *J* = 7.2 Hz, 6 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.33 (br sextet, *J* = 7.4

Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.54 (br quintet,  $J = 7.2$  Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.07 (br quintet,  $J = 6.8$  Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.43 (t,  $J = 6.8$  Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.52-3.55 (m, 4 H, OCH<sub>2</sub>), 3.58-3.65 (m, 16 H, OCH<sub>2</sub>), 4.33 (br t,  $J = 7.0$  Hz, 4 H, NCH<sub>2</sub>), 8.71 (d,  $J = 8.4$  Hz, 2 H, Ar-*H*), 8.93 (s, 2 H, Ar-*H*), 9.50 (d,  $J = 8.4$  Hz, 2 H, Ar-*H*). Approximately 15% of the isomeric **1,6-PBr<sub>2</sub>R**, which could not be separated, was indicated by doublet, singlet and doublet signals at  $\delta$  8.72, 8.93 and 9.51, respectively. MS (MALDI-TOF): found, 950.7, 953.2; calcd for C<sub>46</sub>H<sub>52</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>10</sub>, 952.73.

**1-Bromo-*N,N'*-bis[3-[2-[2-(butoxy)ethoxy]ethoxy]propyl]perylene-3,4,9,10-tetracarboxydiimide (PBr<sub>1</sub>R)**. As described for the preparation of **PBr<sub>2</sub>R**, reaction of **RNH<sub>2</sub>** with the above prepared 1:2:3 inseparable mixture of dianhydrides **PTCDA**, **PBr<sub>1</sub>** and **PBr<sub>2</sub>** resulted in a mixture of perylene diimides that was difficult to separate. Chromatography on neutral alumina (1% methanol in methylene chloride eluent) removed **PPEEB** and yielded 71% of an approximately 3:5 mixture of **PBr<sub>1</sub>R** and **PBr<sub>2</sub>R**, respectively. Preparative TLC on silica gel (5% methanol in methylene chloride eluent) provided pure samples of **PBr<sub>1</sub>R**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.89 (t,  $J = 7.2$  Hz, 6 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.33 (br sextet,  $J = 7.4$  Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.54 (br quintet,  $J = 7.2$  Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.04-2.10 (m, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.42 (br t,  $J = 6.6$  Hz, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.52-3.55 (m, 4 H, OCH<sub>2</sub>), 3.58-3.66 (m, 16 H, OCH<sub>2</sub>), 4.30-4.36 (m, 4 H, NCH<sub>2</sub>), 8.63 (br d,  $J = 8.0$  Hz, 2 H, Ar-*H*), 8.72 (br d,  $J = 8.0$  Hz, 3 H, Ar-*H*), 8.95 (s, 1 H, Ar-*H*), 9.81 (d,  $J = 8.2$  Hz, 1 H, Ar-*H*). MS (MALDI-TOF): found, 873.3, 875.3; calcd for C<sub>46</sub>H<sub>53</sub>BrN<sub>2</sub>O<sub>10</sub>, 873.84.

**3-[2-(2-Butoxyethoxy)]ethoxy]-1-propanamine (RNH<sub>2</sub>)**. Cyanoethylation of commercially available diethylene glycol butyl ether according to our previously reported procedure<sup>2</sup> afforded a 99% yield of 3-[2-(2-butoxyethoxy)]ethoxy]propanenitrile (**RCN**). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.92 (t,  $J = 7.4$  Hz, 3 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.36 (br sextet,  $J = 7.6$  Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.57 (br quintet,  $J = 7.6$  Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.62 (t,  $J = 6.6$  Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CN), 3.46 (t,  $J = 6.6$  Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.57-3.60 (m, 2 H, OCH<sub>2</sub>), 3.64-3.68 (m, 6 H, OCH<sub>2</sub>), 3.74 (br t,  $J = 6.6$  Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CN). Hydrogenation of **RCN**



according to our previously reported procedure<sup>2</sup> produced **RNH<sub>2</sub>** in 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.92 (t, *J* = 7.4 Hz, 3 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.36 (br sextet, *J* = 7.6 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.57 (br quintet, *J* = 7.6 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.82 (quintet, *J* = 6.4 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.91 (t, *J* = 6.4 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.35 (br s, 2 H, NH<sub>2</sub>, exchanges with D<sub>2</sub>O), 3.48 (t, *J* = 6.8 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.57-3.66 (m, 10 H, OCH<sub>2</sub>).

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