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High-purity, symmetrically substituted perylene and naphthalene bisimides were obtained by hydrothermal condensation of monoamines with the corresponding bisanhydride. The hydrothermal imidization proceeds quantitatively, without the need for organic solvents, catalysts or excess of the amines.

The development of chemical reactions that minimize environmental impact, as expressed by the principles of “green chemistry”, is currently one of the major challenges in synthetic chemistry.¹ This effort is even more important for (i) widely encountered chemical functions, (ii) that are typically only accessible *via* harsh and harmful synthetic procedures. The imide aka diacyl amide function is among such omnipresent chemical moieties. Imides are widely used as protecting groups (*e.g.* phthalimides²), for bioconjugation reactions (*e.g.* maleimide–thiol coupling^{3–5}), in polymer chemistry (*e.g.* polyimides,^{6,7} maleimide resins⁸), as dyes (*e.g.* perylene (PBIs) and naphthalene bisimides (NBIs)),^{9–11} and chromonic liquid crystals (perylene bisimide derivatives).^{12–14} The molecular features generating PBIs’ and NBIs’ dye properties, *i.e.* aromatic π -systems, also enable energy and electron transfer ability, and allow for the formation of intriguing supramolecular assemblies.^{10,11} Symmetrically *N*-substituted NBIs and PBIs are most commonly synthesized by (i) Langhals’ method consisting of condensing the naphthalene (NBA) or perylene bisanhydride (PBA) with the respective monoamine in molten imidazole (or quinoline) employing zinc acetate or dicyclohexylcarbodiimide as promotor at high temperatures (180–230 °C).^{15–18} (ii) Moreover, the addition of Zn salts can be omitted using aprotic polar

Green and highly efficient synthesis of perylene and naphthalene bisimides in nothing but water†

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solvents (*e.g.* DMF) at high temperatures.^{11,19} Scarcely used alternative routes include the thermal solid-state condensation of co-crystals of NBA and amines at 160 °C,²⁰ and direct approaches between bisanhydride and the liquid amine using acetic acid as promotor.^{21,22} While these techniques, especially Langhals’ method, generate NBIs and PBIs in high yields, the products have to be purified chromatographically or by recrystallization. Moreover, typically 4-fold (in some cases up to 20-fold) molar excess of the monoamines are used, which is highly undesirable in terms of “green chemistry”. Clearly, for both NBIs and PBIs, these most common syntheses can be qualified as toxic and harsh. We recently reported that fully aromatic polyimides can be synthesized by so-called hydrothermal polymerization (HTP).²³ Here, the imide functions are obtained by condensation of aromatic diamines with aromatic dianhydrides (or tetracarboxylic acids) in water at > 180 °C and autogenous pressures. For instance, at 180–200 °C, the autogenous pressure of H₂O is of only 12–17 bar. These rather moderate conditions can be generated easily in commercial autoclaves and do not require custom-made set-ups. In the hydrothermal regime, H₂O becomes increasingly apolar and at the same time shows an increase in its ionic product, *i.e.* the concentration of both OH[−] and H₃O⁺ ions increases, enabling the medium itself to act as both an acid and a base catalyst, which is indeed beneficial for organic condensations.²⁴ These findings prompted us to investigate if HTP conditions could also be applied to small organic molecules.

In this contribution, we report a novel, green technique to prepare symmetrically substituted PBIs and NBIs in nothing but water. First, we reacted a series of eleven *n*-alkyl monoamines (*n*-C_{*n*}-NH₂) with PBA (Fig. 1). Specifically, we employed *n*-C₅-, *n*-C₆-, *n*-C₇-, *n*-C₈-, *n*-C₉-, *n*-C₁₀-, *n*-C₁₁-, *n*-C₁₂-, *n*-C₁₄-, *n*-C₁₅-, *n*-C₁₆- and *n*-C₁₈-NH₂. Therefore, 1 eq. of PBA and 2 eq. of *n*-C_{*n*}-NH₂ were stirred in deionized water (*c* = 0.03 mol L^{−1}) at RT for 15 min. The resulting suspension was transferred to a non-stirred autoclave that was placed into an oven preheated at 200 °C. After 24 h, the autoclave was allowed to slowly cool back to RT, and the crude product was isolated by filtration, but not subjected to any further purification such as conventional recrystallization or chromatographic separation.

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Fig. 3 $^1\text{H-NMR}$ spectra (600 MHz, CDCl_3/TFA : 5/1 v/v, 16 scans) of $n\text{-C}_n\text{-PBIs}$ synthesized hydrothermally at $200\text{ }^\circ\text{C}$ for 24 h; black = $n\text{-C}_{14}\text{-PBI}$, turquoise = $n\text{-C}_8\text{-PBI}$. Solvent residual peak (7.26 ppm) is marked with *.

$n\text{-C}_{16}$ - and $n\text{-C}_{18}$ -PBI, we did not find residual amines in NMR (ESI †), despite the incompleteness, judged from ATR-FTIR, of the transformation in both cases. We believe, that the remaining amine was dissolved/dispersed in the aqueous supernatant after the HT transformation, most likely in its ammonium form. Note that selected $n\text{-C}_n\text{-PBI}$ were additionally confirmed by mass spectrometry (ESI †).

Soluble PBIs find tremendous interest for energy-related applications, e.g. in the field of organic electronics, and as fluorescence dyes.¹⁰ In both cases, their solubility is required for processing, and their purity is of prime importance. For testing the dye quality, we performed UV-Vis absorption and fluorescence measurements in CH_2Cl_2 and CHCl_3 . The UV-Vis and the fluorescence spectrum of $n\text{-C}_{14}\text{-PBI}$ are exemplarily shown in Fig. 4 (see ESI † for spectra of all other $n\text{-C}_n\text{-PBIs}$). Both the absorption maxima (526 nm, 490 nm, 458 nm) and the fluorescence maxima (533 nm, 574 nm, 624 nm) are in good agreement with the literature.⁹ The fluorescence quantum yields of all measured $n\text{-C}_n\text{-PBIs}$ are $\Phi_F \approx 1$ (see ESI †). All $n\text{-C}_n\text{-PBIs}$ are soluble in a number of organic solvents (CH_2Cl_2 , CHCl_3 , DMSO, DMF, benzene, nitrobenzene, in the mg/100 mL range) generating strongly colored, translucent solutions (Fig. 4, ESI †). Since the fluorescence can be affected by impurities that also show fluorescence, such as aromatics/heteroaromatics, the hydrothermal imide synthesis presented here is clearly preferable to condensations in imidazole, especially since it requires no purification.

While all hydrothermally prepared $n\text{-C}_n\text{-PBIs}$ have previously been prepared by conventional methods by others, not all of

them had been fully characterized. As a positive side effect, the fact that hydrothermal synthesis allowed us to rapidly synthesize this entire series of $n\text{-C}_n\text{-PBIs}$, we could add a considerable amount of to date unreported experimental data on these compounds (see comparison table, ESI †).

Having shown that symmetrically n -alkyl-substituted PBIs can be obtained quantitatively and with great purity within 24 h at $200\text{ }^\circ\text{C}$ in H_2O , we were interested in studying if: (i) hydrothermal conditions were necessary, or if condensation could also be achieved in H_2O at reflux; (ii) If the method was also applicable to other amines (different $\text{p}K_a$ -values, different steric demands) and (iii) to other bisanhydrides (specifically NBA); and lastly (iv) the completeness and reaction time could be improved adding a non-nucleophilic base as condensation promotor.

To probe if $n\text{-C}_n\text{-PBIs}$ would be obtainable in H_2O at reflux, we took a closer look at 4 PBIs of different polarity and hence solubility of both the monoamine and the resulting PBI: $n\text{-C}_5$, $n\text{-C}_{11}$, $n\text{-C}_{14}$ and $n\text{-C}_{18}$ -PBI. The conversion to the PBIs was tested by ATR-FTIR, after reaction times of 2, 4, 6, 24 and 72 h. In all cases, the $n\text{-C}_n\text{-PBIs}$ are forming in considerable amounts, but even after 72 h we still find remaining PBA (ESI †). Therefrom, it can be concluded that HT conditions are indeed required for quantitative yields after reasonable reaction times when equimolar amounts of the starting compounds are employed. Note that Tam-Chang *et al.* could obtain a perylene monoimide potassium carboxylate, by stirring the parent monoanhydride potassium salt with N,N -diethylethylenediamine in ambient water.¹⁴ However, their approach is limited to employing an excess of water-soluble amines in combination with the increased solubility of the monoanhydride potassium salt compared to PBA.

Hydrothermal bisimide syntheses additionally employing Hünig's base (N,N -diisopropylethylamine, HB) as non-nucleophilic base, and/or starting from NBA and/or other amines (cyclohexylamine ($c\text{-C}_6\text{-NH}_2$), aniline (An)) are summarized in Table 1 (ESI † for corresponding ATR-FTIR). First, for $n\text{-C}_n\text{-PBIs}$, it becomes clear that the addition of 1–2 drops of HB allows for reducing the reaction time needed for quantitative yield ($t_{R,q}$) from 24 h (no HB) to 4 h for both $n\text{-C}_8$ - and $n\text{-C}_{14}$ -PBI (Table 1, entries 01–04). However, $n\text{-C}_{18}$ -PBI could not be obtained quantitatively by adding HB (Table 1, entry 06). Nonetheless, the consumption of PBA was much improved by the HB addition (ESI † , ATR-FTIR). Second, $n\text{-C}_n\text{-NBIs}$ were readily obtainable already without the addition of HB: $t_{R,q} \approx 16$ h was sufficient to generate $n\text{-C}_8\text{-NBI}$ without HB, which compares to $t_{R,q} \approx 24$ h for $n\text{-C}_8\text{-PBI}$ (Table 1, entries 10 and 01). We attribute this to the increased solubility of NBA in H_2O in the HT regime compared to PBA. For $n\text{-C}_8\text{-NBI}$, addition of HB significantly reduced $t_{R,q}$ by a factor of 4, to 4 h (Table 1, entry 11). Most interestingly, $n\text{-C}_{18}\text{-NBI}$ was obtained quantitatively after $t_{R,q} \approx 16$ h, without HB (Table 1, entry 12). Given the high water-insolubility of $n\text{-C}_{18}\text{-NH}_2$, which did not allow for obtaining $n\text{-C}_{18}\text{-PBI}$ at any tested conditions, this result is most impressive. Third, cyclohexyl-disubstituted PBI and NBI were obtained quantitatively only in the presence of HB (Table 1, entries 07, 08, 13 and 14), *i.e.* after only 4 h for $c\text{-C}_6\text{-PBI}$ and 16 h for $c\text{-C}_6\text{-NBI}$. While the $\text{p}K_a$ of $c\text{-C}_6\text{-NH}_2$ (≈ 10.6) is not significantly different from that of $n\text{-C}_n\text{-NH}_2$ (≈ 10.4), cyclohexylamine is

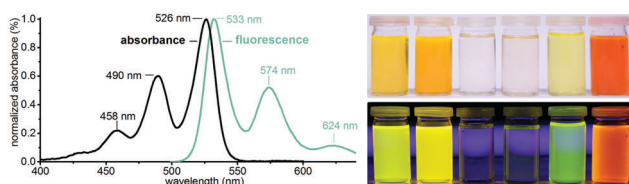


Fig. 4 Left: UV-Vis (black) and fluorescence (turquoise) spectrum of $n\text{-C}_{14}\text{-PBI}$ in CH_3Cl synthesized hydrothermally at $200\text{ }^\circ\text{C}$ for 24 h. Right: Aspect of $n\text{-C}_{14}\text{-PBI}$ under visible (top) and UV-light (bottom) in the solvents (from left to right): CHCl_3 , CH_2Cl_2 , DMF, DMSO, THF, TFA.



