

# ChemComm

Chemical Communications

rsc.li/chemcomm



ISSN 1359-7345



**COMMUNICATION**

Miriam M. Unterlass *et al.*

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



Cite this: *Chem. Commun.*, 2017, 53, 1229

Received 9th August 2016,  
Accepted 21st November 2016

DOI: 10.1039/c6cc06567h

www.rsc.org/chemcomm

**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.<sup>1</sup> 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.* phthalimides<sup>2</sup>), for bioconjugation reactions (*e.g.* maleimide–thiol coupling<sup>3–5</sup>), in polymer chemistry (*e.g.* polyimides,<sup>6,7</sup> maleimide resins<sup>8</sup>), as dyes (*e.g.* perylene (PBIs) and naphthalene bisimides (NBIs)),<sup>9–11</sup> and chromonic liquid crystals (perylene bisimide derivatives).<sup>12–14</sup> The molecular features generating PBIs’ and NBIs’ dye properties, *i.e.* aromatic  $\pi$ -systems, also enable energy and electron transfer ability, and allow for the formation of intriguing supramolecular assemblies.<sup>10,11</sup> 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).<sup>15–18</sup> (ii) Moreover, the addition of Zn salts can be omitted using aprotic polar

solvents (*e.g.* DMF) at high temperatures.<sup>11,19</sup> Scarcely used alternative routes include the thermal solid-state condensation of co-crystals of NBA and amines at 160 °C,<sup>20</sup> and direct approaches between bisanhydride and the liquid amine using acetic acid as promotor.<sup>21,22</sup> 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).<sup>23</sup> 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 H<sub>2</sub>O 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, H<sub>2</sub>O becomes increasingly apolar and at the same time shows an increase in its ionic product, *i.e.* the concentration of both OH<sup>−</sup> and H<sub>3</sub>O<sup>+</sup> ions increases, enabling the medium itself to act as both an acid and a base catalyst, which is indeed beneficial for organic condensations.<sup>24</sup> 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<sub>*n*</sub>-NH<sub>2</sub>) with PBA (Fig. 1). Specifically, we employed *n*-C<sub>5</sub>-, *n*-C<sub>6</sub>-, *n*-C<sub>7</sub>-, *n*-C<sub>8</sub>-, *n*-C<sub>9</sub>-, *n*-C<sub>10</sub>-, *n*-C<sub>11</sub>-, *n*-C<sub>12</sub>-, *n*-C<sub>14</sub>-, *n*-C<sub>15</sub>-, *n*-C<sub>16</sub>- and *n*-C<sub>18</sub>-NH<sub>2</sub>. Therefore, 1 eq. of PBA and 2 eq. of *n*-C<sub>*n*</sub>-NH<sub>2</sub> were stirred in deionized water (*c* = 0.03 mol L<sup>−1</sup>) 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.

<sup>a</sup> Technische Universität Wien, Institute of Materials Chemistry, Getreidemarkt 9/BC/2, A-1060 Vienna, Austria. E-mail: miriam.unterlass@tuwien.ac.at; Fax: +43-(0)1-58801-165981; Tel: +43-(0)1-58801-165206

<sup>b</sup> Technische Universität Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-IAC, 1060 Vienna, Austria

<sup>c</sup> Technische Universität Wien, Institute of Applied Synthetic Chemistry, Getreidemarkt 9/163, 1060 Vienna, Austria

† Electronic supplementary information (ESI) available: Materials & methods, ATR-FTIR, SEM, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, MALDI-TOF-MS, UV-Vis, fluorescence, PXRD. See DOI: 10.1039/c6cc06567h





Fig. 1 Hydrothermal condensations of NBIs and PBIs: the dianhydrides NBA and PBA are reacted with different monoamines in equimolar ratio (1:2, no excess of  $\text{RNH}_2$ ). HTW = high-temperature water, here: 200 °C and autogenous pressure.

Note that all  $n\text{-C}_n\text{-PBI}$  products, except  $n\text{-C}_{16}\text{-PBI}$  and  $n\text{-C}_{18}\text{-PBI}$ , were obtained quantitatively. In the ATR-FTIR spectra of  $n\text{-C}_n\text{-PBIs}$  (ESI†), we find the for PBIs characteristic imide modes ( $1693\text{ cm}^{-1}$  and  $1654\text{ cm}^{-1}$ ). Moreover, the  $\text{NH}_2$  modes of the  $n\text{-alkylamines}$  ( $\tilde{\nu}(\text{N-H})$  and intermolecular H-bonding of amine groups  $\approx 3330\text{--}3200\text{ cm}^{-1}$ , 2–3 modes) are fully absent in all cases.  $n\text{-C}_5\text{-PBI}$ ,  $n\text{-C}_8\text{-PBI}$ ,  $n\text{-C}_9\text{-PBI}$ ,  $n\text{-C}_{10}\text{-PBI}$ ,  $n\text{-C}_{14}\text{-PBI}$  and  $n\text{-C}_{15}\text{-PBI}$  show no remaining anhydride modes ( $\tilde{\nu}_{\text{as}}(\text{C=O}) \approx 1772\text{ cm}^{-1}$ ,  $\tilde{\nu}_{\text{s}}(\text{C=O}) \approx 1733\text{ cm}^{-1}$ ) related to unreacted PBA. Hence, ATR-FTIR analysis indicates both the full consumption of PBA and the absence of perylene monoimide monoanhydride, which would in principle be a possible product. Indeed, Nagao & Misono and Huang *et al.* have used  $\text{H}_2\text{O}/\text{ROH}$  mixtures as solvents for the synthesis of perylene monoimide monoanhydrides, which were in both cases the major products ( $\approx 80\%$ ), and PBIs only formed in minority ( $\approx 20\%$ ).<sup>25,26</sup> Given that these reports (and also Langhals' method) employ important excesses of the monoamines, it is most fascinating that fully condensed PBIs can be obtained hydrothermally without any additives at equimolar reactant ratio.

While the ATR-FTIR spectra of  $n\text{-C}_6\text{-PBI}$ ,  $n\text{-C}_7\text{-PBI}$ ,  $n\text{-C}_{11}\text{-PBI}$  and  $n\text{-C}_{12}\text{-PBI}$  show very small remaining  $\text{C=O}$  anhydride modes,  $n\text{-C}_{16}\text{-PBI}$  and  $n\text{-C}_{18}\text{-PBI}$  show considerable anhydride modes (see ESI†). The incompleteness of formation of the latter two PBIs is however not related to the basicity of  $n\text{-C}_{16}\text{-PBI}$  and  $n\text{-C}_{18}\text{-PBI}$ , since the  $\text{pK}_a$  values of  $n\text{-alkylamines}$  generally do not vary for different alkyl substituents, but all lie in the same range (10.4–10.6).<sup>27,28</sup> The water-solubility is however strongly decreasing with increasing alkyl chainlength. Therefore, we suppose that the hydrothermal formations of  $n\text{-C}_{16}\text{-PBI}$  and  $n\text{-C}_{18}\text{-PBI}$  are less complete after 24 h, because of  $n\text{-C}_{16}\text{-PBI}$  and  $n\text{-C}_{18}\text{-PBI}$ 's limited solubility in  $\text{H}_2\text{O}$ , and thus limited availability for reaction. The increase in apolarity of the  $n\text{-alkylamines}$  and hence also of the  $n\text{-C}_n\text{-PBIs}$  is indeed reflected by the aspect of the reaction mixtures after hydrothermal imidization: while the  $n\text{-C}_n\text{-PBIs}$  bearing short alkyl chains result as homogeneous dispersions, longer alkyl tails lead to a precipitate covered by a translucent aqueous phase. Specifically,  $n\text{-C}_5$  to  $n\text{-C}_8\text{-PBI}$  are obtained as bright blood-red dispersions with no visible phase separation (photographs, see ESI†).  $n\text{-C}_9$  and  $n\text{-C}_{10}\text{-PBI}$  form a ruby-red colored precipitate covered by a turbid red dispersion, and from  $n\text{-C}_{11}\text{-PBI}$  onwards, the PBIs fully precipitate as brownish-red powders, covered by a translucent yellowish aqueous phase (ESI†).

Micromorphological investigations *via* scanning electron microscopy (SEM) confirm this trend:  $n\text{-C}_5\text{-PBI}$  and  $n\text{-C}_6\text{-PBI}$  are cuboid-like particles of *ca.* 5–10  $\mu\text{m}$  in length and 1–2  $\mu\text{m}$  in



Fig. 2 SEM images of hydrothermally synthesized PBIs and PBA. (A) Hydrothermally treated PBA (24 h, 200 °C). (B–D)  $n\text{-C}_n\text{-PBIs}$  obtained hydrothermally (24 h, 200 °C). B =  $n\text{-C}_5\text{-PBI}$ , C =  $n\text{-C}_8\text{-PBI}$ , D =  $n\text{-C}_{12}\text{-PBI}$ .

thickness (see Fig. 2B and ESI†). In  $n\text{-C}_7\text{-PBI}$  and  $n\text{-C}_8\text{-PBI}$  roundish aggregates of *ca.* 10–50  $\mu\text{m}$  in diameter coexist with ribbons of *ca.* 10  $\mu\text{m} \times 100\text{ nm} \times 1\text{ }\mu\text{m}$  (length  $\times$  thickness  $\times$  depth) (see Fig. 2C and ESI†).  $n\text{-C}_9$  to  $n\text{-C}_{15}\text{-PBI}$  all form stacks of discoid platelets that are each *ca.* 5  $\mu\text{m}$  in diameter and *ca.* 100 nm in thickness (see Fig. 2D and ESI†). For longer alkyl-chains in  $n\text{-C}_n\text{-PBIs}$ , the increased hydrophobicity generates the compounds' drive to limit the contact with the polar medium  $\text{H}_2\text{O}$ : the hydrothermally formed PBIs minimize their surface area for a given volume by adopting roundish morphologies. In contrast, PBIs bearing short alkyl chains do not adopt such roundish morphologies:  $n\text{-C}_5\text{-PBI}$  and  $n\text{-C}_6\text{-PBI}$  resemble the morphology of hydrothermally recrystallized PBA that we prepared for comparison (see Fig. 2A and ESI†). Overall, it can be stated that the PBI morphology is strongly influenced by the  $N\text{-alkyl}$  substitution.

Despite the roundish morphologies found in  $n\text{-C}_7$  to  $n\text{-C}_{15}$ , all PBIs are highly crystalline as evinced by powder X-ray diffraction (PXRD) measurements (ESI†). Since hydrothermal synthesis has been shown to yield outstanding crystallinity for polyimides,<sup>23,24,29</sup> this result comes as no surprise.  $n\text{-C}_{16}\text{-PBI}$  and  $n\text{-C}_{18}\text{-PBI}$  are also highly crystalline in PXRD, but their incompleteness of reaction (especially for  $n\text{-C}_{18}\text{-PBI}$ ) is further underlined by the presence of reflections corresponding to PBA (ESI†).

The  $N\text{-substitution}$  of PBIs with alkyl chains is a means to increase their solubility in organic solvents. Therefore, the  $n\text{-C}_n\text{-PBIs}$  could be analyzed by solution NMR for estimating their purity. Representative  $^1\text{H-NMR}$  spectra of  $n\text{-C}_8\text{-PBI}$  and  $n\text{-C}_{14}\text{-PBI}$  are shown in Fig. 3 (see ESI† for larger representation and spectra of the other  $n\text{-C}_n\text{-PBIs}$ ). Both spectra show all expected peaks and the found integral ratios correspond well to the theoretical ratios ( $n\text{-C}_8\text{-PBI}$ ,  $H_a:H_b:H_c:H_d:H_e$  expected: 6:20:4:4:8, found: 6.14:21.32:3.92:4.00:8.00;  $n\text{-C}_{14}\text{-PBI}$ ,  $H_a:H_b:H_c:H_d:H_e$  expected: 6:44:4:4:8, found: 6.21:47.16:3.87:4.11:8.00). While PBA is insoluble in the solvent used for NMR measurements ( $\text{CDCl}_3/\text{trifluoroacetic acid}$ , 5/1 v/v), remaining monoamine would affect the integrals corresponding to  $\text{CH}_2$  and  $\text{CH}_3$  groups ( $H_a$ ,  $H_b$  and  $H_c$ ). It becomes clear from Fig. 3 that there is no unreacted monoamine present. Note that even for



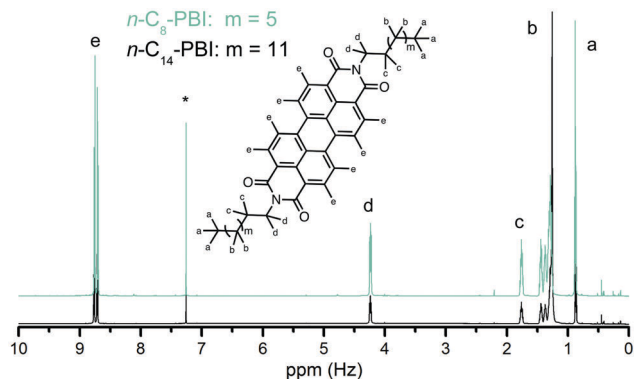


Fig. 3  $^1\text{H-NMR}$  spectra (600 MHz,  $\text{CDCl}_3/\text{TFA}$ : 5/1 v/v, 16 scans) of  $n\text{-C}_n\text{-PBIs}$  synthesized hydrothermally at  $200\text{ }^\circ\text{C}$  for 24 h; black =  $n\text{-C}_{14}\text{-PBI}$ , turquoise =  $n\text{-C}_8\text{-PBI}$ . Solvent residual peak (7.26 ppm) is marked with \*.

$n\text{-C}_{16}\text{-}$  and  $n\text{-C}_{18}\text{-PBI}$ , we did not find residual amines in NMR (ESI $^\dagger$ ), 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 $^\dagger$ ).

Soluble PBIs find tremendous interest for energy-related applications, e.g. in the field of organic electronics, and as fluorescence dyes.<sup>10</sup> 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  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ . The UV-Vis and the fluorescence spectrum of  $n\text{-C}_{14}\text{-PBI}$  are exemplarily shown in Fig. 4 (see ESI $^\dagger$  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.<sup>9</sup> The fluorescence quantum yields of all measured  $n\text{-C}_n\text{-PBIs}$  are  $\Phi_F \approx 1$  (see ESI $^\dagger$ ). All  $n\text{-C}_n\text{-PBIs}$  are soluble in a number of organic solvents ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , DMSO, DMF, benzene, nitrobenzene, in the mg/100 mL range) generating strongly colored, translucent solutions (Fig. 4, ESI $^\dagger$ ). 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 $^\dagger$ ).

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  $\text{H}_2\text{O}$ , we were interested in studying if: (i) hydrothermal conditions were necessary, or if condensation could also be achieved in  $\text{H}_2\text{O}$  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  $\text{H}_2\text{O}$  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  $n\text{-C}_{18}\text{-PBI}$ . 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 $^\dagger$ ). 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.<sup>14</sup> 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 $^\dagger$  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  $n\text{-C}_8\text{-}$  and  $n\text{-C}_{14}\text{-PBI}$  (Table 1, entries 01–04). However,  $n\text{-C}_{18}\text{-PBI}$  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 $^\dagger$ , 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  $\text{H}_2\text{O}$  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  $c\text{-C}_6\text{-NH}_2$  ( $\approx 10.6$ ) is not significantly different from that of  $n\text{-C}_n\text{-NH}_2$  ( $\approx 10.4$ ), cyclohexylamine is

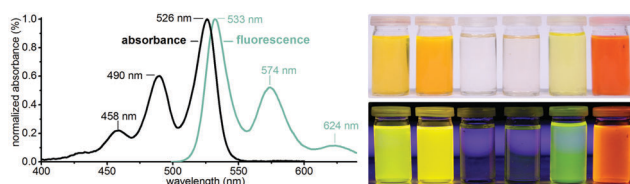


Fig. 4 Left: UV-Vis (black) and fluorescence (turquoise) spectrum of  $n\text{-C}_{14}\text{-PBI}$  in  $\text{CH}_3\text{Cl}$  synthesized hydrothermally at  $200\text{ }^\circ\text{C}$  for 24 h. Right: Aspect of  $n\text{-C}_{14}\text{-PBI}$  under visible (top) and UV-light (bottom) in the solvents (from left to right):  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , DMF, DMSO, THF, TFA.



**Table 1** Various NBI and PBI syntheses. All reactions were carried out at 200 °C and equimolar anhydride:amine ratio. *c*-C<sub>6</sub>-NH<sub>2</sub> = cyclohexylamine ( $pK_a(c\text{-C}_6\text{-NH}_2) \approx 10.6$ ), An = Aniline ( $pK_a(\text{An}) \approx 4.6$ ), HB = Hünig's base,  $t_{R,q}$  = reaction time until bisimides were obtained quantitatively

Entry	Bisanhydride	Monoamine	HB	$t_{R,q}$ [h]
01	PBA	<i>n</i> -C <sub>8</sub> -NH <sub>2</sub>	—	24
02	PBA	<i>n</i> -C <sub>8</sub> -NH <sub>2</sub>	y	4
03	PBA	<i>n</i> -C <sub>14</sub> -NH <sub>2</sub>	—	24
04	PBA	<i>n</i> -C <sub>14</sub> -NH <sub>2</sub>	y	4
05 <sup>a</sup>	PBA	<i>n</i> -C <sub>18</sub> -NH <sub>2</sub>	—	> 24
06 <sup>a,b</sup>	PBA	<i>n</i> -C <sub>18</sub> -NH <sub>2</sub>	y	> 17
07 <sup>a</sup>	PBA	<i>c</i> -C <sub>6</sub> -NH <sub>2</sub>	—	> 24
08	PBA	<i>c</i> -C <sub>6</sub> -NH <sub>2</sub>	y	17
09 <sup>a,b</sup>	PBA	An	y	> 17
10	NBA	<i>n</i> -C <sub>8</sub> -NH <sub>2</sub>	—	16
11	NBA	<i>n</i> -C <sub>8</sub> -NH <sub>2</sub>	y	4
12	NBA	<i>n</i> -C <sub>18</sub> -NH <sub>2</sub>	—	16
13 <sup>a</sup>	NBA	<i>c</i> -C <sub>6</sub> -NH <sub>2</sub>	—	> 17
14	NBA	<i>c</i> -C <sub>6</sub> -NH <sub>2</sub>	y	4
15	NBA	An	—	17

<sup>a</sup> Not complete after longest tested reaction time. <sup>b</sup> Considerably higher anhydride consumption than without HB; y = 1–2 drops of HB were added to the reaction.

less nucleophilic due to its steric hindrance.<sup>30</sup> This is a possible explanation for the need to add HB for quantitative imidization of both NBA and PBA. Lastly, we tested aniline (An) as monoamine, which is much less basic ( $pK_a \approx 4.6$ ) than the used alkylamines, and also a weak nucleophile through the mesomeric effect.<sup>30</sup> While An-PBI could not be obtained quantitatively after the longest tested  $t_R$  of 17 h even with HB (Table 1, entry 10), An-NBI was obtained quantitatively without HB after 17 h. This is again most likely related to the higher solubility of NBA compared to PBA, in the HT regime. Clearly, for all employed amines and both bisanhydrides, the speed and completion of the hydrothermal condensation are directly related to the solubility of the starting compounds, their polarity, and nucleophilicity and basicity of the employed amines. Hence, if aiming at *N*-substituents of the swallow tail or perfluoro-alkyl type – which are of high interest to PBI and NBI dye applications – it is exactly these factors that will have to be considered.

In summary, we have prepared a series of high-purity, symmetrically substituted PBIs and NBIs in nothing but water at hydrothermal conditions. The hydrothermal imidization lies in stark contrast to conventional techniques, as: (i) no toxic solvents or catalysts are required at all, (ii) starting compounds were used in stoichiometric amounts, and (iii) no purification (such as recrystallization or chromatography) is required. Moreover, the reactions were complete after reasonable reaction times (max. 24 h) at quantitative yields, with the exception of very hydrophobic amines (*n*-C<sub>16</sub>- and *n*-C<sub>18</sub>-PBI), and could be accelerated by adding a non-nucleophilic base. Lastly, NBIs are generally more readily formed hydrothermally than PBIs, which we

attribute to the increased solubility of NBA in the hydrothermal regime. Our approach presents a rapid and easy means for accessing symmetrically substituted PBIs, which we believe to be of high interest – especially to non-chemists – for the application of these compounds in *e.g.* energy-related applications.

The authors acknowledge TU Wien for funding this project, and are grateful to Maximilian Raab for preliminary experiments. Powder X-ray diffraction measurements were carried out at the X-ray Center of TU Wien (XRC), and SEM was carried out at the interfaculty electron microscopy facility of TU Wien (USTEM).

## References

- M. Poliakoff and P. Licence, *Nature*, 2007, **450**, 810–812.
- P. Y. Reddy, S. Kondo, T. Toru and Y. Ueno, *J. Org. Chem.*, 1997, **62**, 2652–2654.
- S. S. Ghosh, P. M. Kao, A. W. McCue and H. L. Chappelle, *Bioconjugate Chem.*, 1990, **1**, 71–76.
- R. J. Pounder, M. J. Stanford, P. Brooks, S. P. Richards and A. P. Dove, *Chem. Commun.*, 2008, 5158–5160.
- A. D. Baldwin and K. L. Kiick, *Bioconjugate Chem.*, 2011, **22**, 1946–1953.
- D.-J. Liaw, K.-L. Wang, Y.-C. Huang, K.-R. Lee, J.-Y. Lai and C.-S. Ha, *Prog. Polym. Sci.*, 2012, **37**, 907–974.
- Y. Liao, J. Weber and C. F. Faul, *Macromolecules*, 2015, **48**, 2064–2073.
- J. C. Phelan and C. S. P. Sung, *Macromolecules*, 1997, **30**, 6845–6851.
- H. Langhals, *Heterocycles*, 1995, **1**, 477–500.
- F. Würthner, *Chem. Commun.*, 2004, 1564–1579.
- S. V. Bhosale, C. H. Jani and S. J. Langford, *Chem. Soc. Rev.*, 2008, **37**, 331–342.
- S.-W. Tam-Chang and L. Huang, *Chem. Commun.*, 2008, 1957–1967.
- I. K. Iverson, S. M. Casey, W. Seo, S.-W. Tam-Chang and B. A. Pindzola, *Langmuir*, 2002, **18**, 3510–3516.
- S.-W. Tam-Chang, W. Seo and I. K. Iverson, *J. Org. Chem.*, 2004, **69**, 2719–2726.
- A. Rademacher, S. Märkle and H. Langhals, *Chem. Ber.*, 1982, **115**, 2927–2934.
- H. Langhals, *Chem. Ber.*, 1985, **118**, 4641–4645.
- P. Gawrys, D. Boudinet, M. Zagorska, D. Djurado, J.-M. Verilhac, G. Horowitz, J. Pécaud, S. Pouget and A. Pron, *Synth. Met.*, 2009, **159**, 1478–1485.
- H. Katz, A. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin and A. Dodabalapur, *Nature*, 2000, **404**, 478–481.
- S. Hünig, J. Groß, E. F. Lier and H. Quast, *Justus Liebigs Ann. Chem.*, 1973, **1973**, 339–358.
- M. L. Cheney, G. J. McManus, J. A. Perman, Z. Wang and M. J. Zaworotko, *Cryst. Growth Des.*, 2007, **7**, 616–617.
- T. Maki and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1954, **27**, 602–605.
- T. Maki and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1952, **25**, 411–413.
- B. Baumgartner, M. J. Bojdys and M. M. Unterlass, *Polym. Chem.*, 2014, **5**, 3771–3776.
- B. Baumgartner, M. J. Bojdys, P. Skrinjar and M. M. Unterlass, *Macromol. Chem. Phys.*, 2016, **217**, 485–500.
- Y. Nagao and T. Misono, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1191–1194.
- H. Huang, Y. Che and L. Zang, *Tetrahedron Lett.*, 2010, **51**, 6651–6653.
- H. Hall and R. B. Bates, *Tetrahedron Lett.*, 2012, **53**, 1830–1832.
- D. D. Perrin, B. Dempsey and E. P. Serjeant, *pKa prediction for organic acids and bases*, Springer, 1981, vol. 1.
- B. Baumgartner, M. Puchberger and M. M. Unterlass, *Polym. Chem.*, 2015, **6**, 5773–5781.
- W. A. Henderson Jr and C. J. Schultz, *J. Org. Chem.*, 1962, **27**, 4643–4646.

