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# Dual role of polyphosphoric acid-activated nitroalkanes in oxidative *peri*-annulations: efficient synthesis of 1,3,6,8-tetraazapyrenes†

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A highly efficient synthetic method for expeditious and selective assembly of tetraazapyrenes (TAPy) is reported, based on the novel reaction of electrophilically activated nitroalkanes with aromatic amines. Remarkably, the nitroalkanes play a dual role in this process, also serving as mild and efficient oxidants promoting aromatization of the final product and allowing for the exclusion of a poorly controllable aerobic treatment.

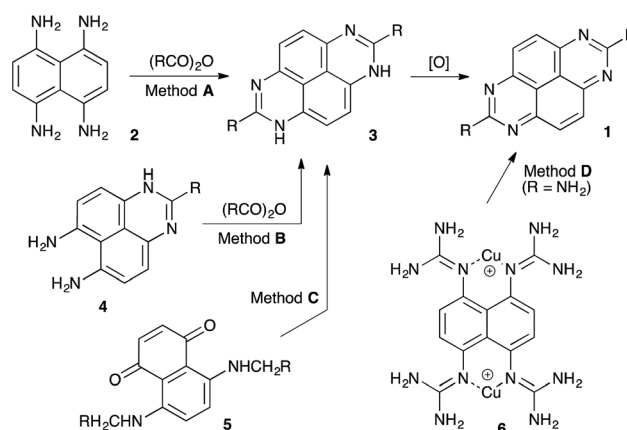
## Introduction

During the past decade, increasing attention of many research groups has been placed on the development of new  $\pi$ -conjugated organic materials for application in electronic and optoelectronic devices, such as light-emitting diodes (LEDs), field-effect transistors (FETs), and efficient and cost-effective solar cells.<sup>1,2</sup> Among other fused polycyclic systems, tetraazapyrenes (TAPy, **1**) have great promise as novel luminescent materials in sensors, lasers, and semi-conductor devices due to their favorable Red-Ox and photochemical properties.<sup>3</sup> However, synthetic approaches to this heterocyclic core are limited to a handful of reliable methods. The most common synthetic route employs a double-fold cyclo-condensation of naphthalene-1,4,5,8-tetraamine (**2**) with carboxylic anhydrides and subsequent oxidation of the intermediate 1,8-dihydropyrimido[4,5,6-*gh*]perimidines **3** (Scheme 1, method A).<sup>3a,b</sup> Alternatively, this protocol could utilize 1*H*-perimidine-6,7-diamines **4** (method B)<sup>4</sup> that are readily accessible *via* Pozharskii's electrophilic nitration approach.<sup>4</sup> More unusual approaches involve thermally induced double-fold cyclo-condensation of 5,8-bis(methylamino)naphthalene-1,4-diones (**5**) (Scheme 1, method C),<sup>5</sup> or oxidative decomposition of dinuclear copper-2,2',2'',2'''-(naphthalene-1,4,5,8-tetrayl)tetraguanidine complexes **6** (method D).<sup>6</sup> Notably, all of these methods rely on an

oxidation step (usually aerobic) that could be substrate-dependent, providing inconsistent results upon scaling up. Herein we wish to report an innovative approach to the TAPy scaffolds, utilizing the nucleophilic reaction of substrates **2** and **4** with umpolung-activated electrophilic nitroalkanes. Remarkably, the latter compounds also serve as oxidizing agents for the aromatization of the target heterocyclic system.

## Results and discussion

For several years our group had a great interest in development novel synthetic approaches towards fused aromatic polyheterocyclic cores targeting material science<sup>7</sup> and medicinal chemistry applications.<sup>8</sup> Several innovative approaches towards TAPy scaffolds were also developed (Scheme 2). These methods involved one-pot double nitration of perimidines followed by zinc-assisted reductive cyclo-condensation with formic acid (method E),<sup>9</sup> and various *peri*-annulation cascades triggered by



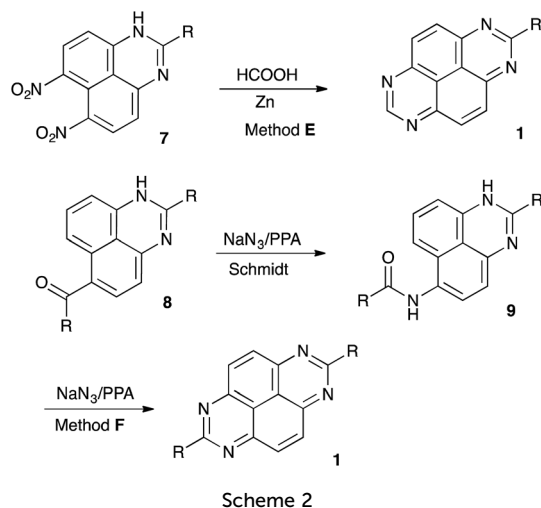
Scheme 1

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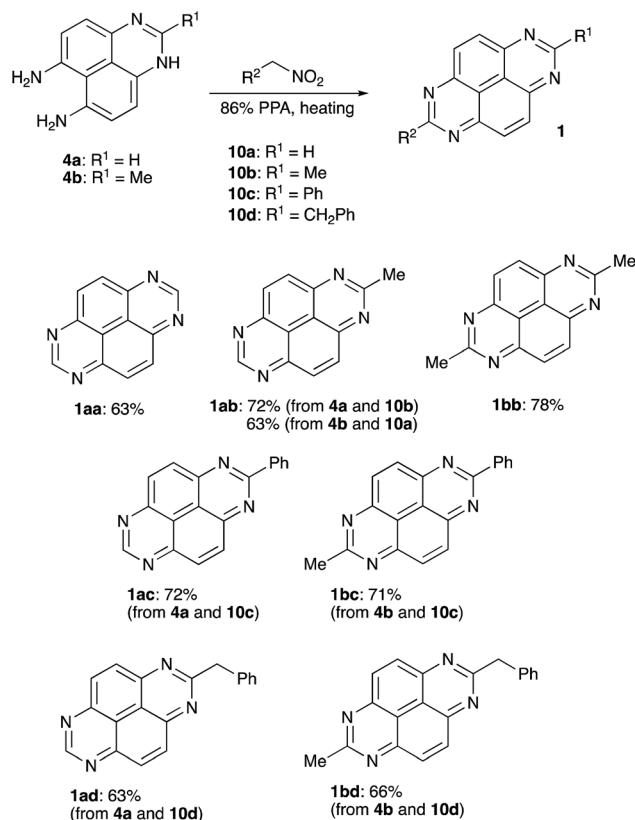
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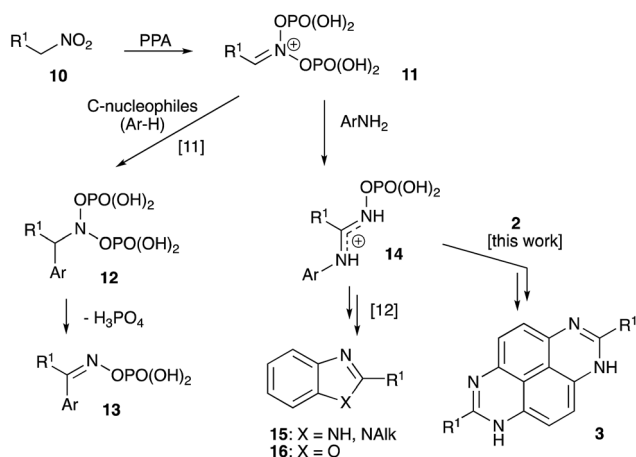
the Schmidt reaction of 6(7)-acylperimidines **8** (Scheme 2) (method F).<sup>10</sup> We also demonstrated that nitroalkanes **10** react with polyphosphoric acid (PPA) to form highly stabilized aci form **11**, which can serve as electrophilic component in highly selective Nef-like processes involving various carbon-<sup>11</sup> and nitrogen-based nucleophiles<sup>12</sup> (Scheme 3). Indeed, reactions of **11** with electron-rich aromatic compounds usually affords phosphorylated *N*-hydroxyhydroxylamine species **12**, possessing a hydrogen atom at  $\alpha$ -position, which undergoes facile elimination of  $\text{H}_3\text{PO}_4$  to furnish phosphorylated oxime **10**. The latter can undergo further Beckman or aza-Wagner–Meerwein rearrangements providing unusual avenues for selective installation of functional groups into aromatic compounds (Scheme 3).<sup>13</sup> Reactions of **11** with nitrogen-based nucleophiles (typically anilines) provide stabilized amidinium ions **14**. Installation of nucleophilic functionality in the strategic position could trigger intramolecular cyclo-condensation. This approach allowed us to develop expeditious synthetic route towards imidazoles **15** and oxazoles **16** (Scheme 3).<sup>14</sup> We envisioned that similar strategy could potentially be employed for

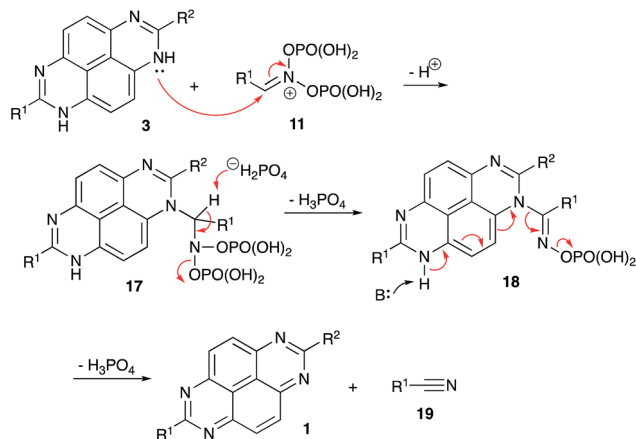


the synthesis of heteroaromatic core **3** (Scheme 3) *via* reaction of nitroalkanes with 1*H*-perimidine-6,7-diamines **4**.

To test this idea we stirred 1*H*-perimidine-6,7-diamine (**4a**) in 86% PPA in the presence of nitromethane (**10a**). Interestingly, we did not observe formation of compound **3** ( $\text{R}^1 = \text{H}$ ). Instead, TAPy (**1aa**) formed as sole product in a yield of 63% (Scheme 4). Due to the symmetry of the scaffold, 2-Me-TAPy (**1ab**) can be assembled in two different way, either starting from **4a** and nitroethane (**10b**) or by combining 2-methyl-1*H*-perimidine-6,7-diamine (**4b**) with nitromethane (**10a**). Both protocols work fine, affording the corresponding product **1ab** in 72% and 63% yield, respectively (Scheme 4). 2,7-Me<sub>2</sub>-TAPy (**1bb**) was synthesized in a similar manner by treatment of **4b** with nitroethane (**10b**). Evidently, a phenyl substituent could be introduced into the target scaffold *via* the reaction of an appropriate perimidine with  $\alpha$ -nitrotoluene (**10c**). Indeed, 2-Ph-TAPy (**1ac**) and 2-Me-7-PhTAPy (**1bc**) were accessed *via* this mode very efficiently (Scheme 4). Finally, (2-nitroethyl)-benzene (**10d**) can be employed for the installation of benzylic substituents. Both tested perimidines **4a** and **4b** afforded the corresponding 7-benzyl-TAPy's **1ad** and **1bd** in good yields (Scheme 4).

As mentioned above, the tetraazopyrenes **1** were obtained in the featured reaction with nitroalkanes directly, and reduced form **3** was never detected in the reaction mixtures. This also was the case even when the annulations were carried out under inert atmosphere to exclude the possibility of aerobic oxidation. We reasoned, that the nitroalkane *aci* form may play here a dual

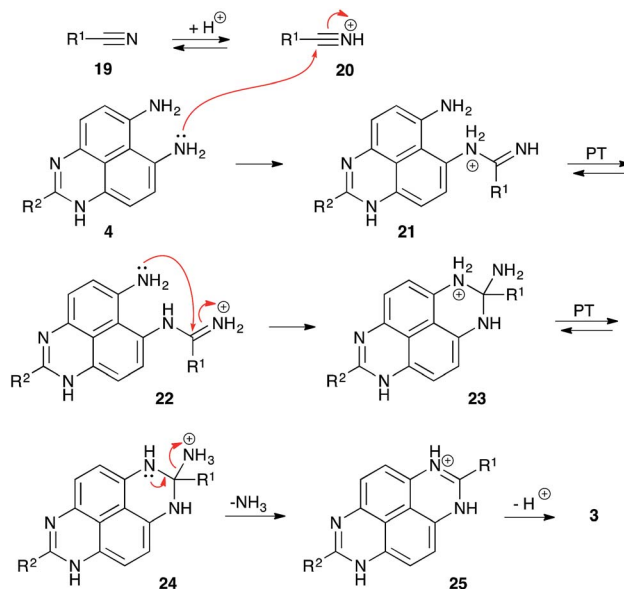




Scheme 5

role, serving both as an electrophilic reagent in cyclization and as an oxidant. Indeed, if we suppose that 1,8-dihydropyrimido [4,5,6-*gh*]perimidine core **3** was formed in the reaction, it also could be involved in nucleophilic attack at the C=N bond of *aci* form **11**. The resulting *N*-(imino-methyl)amidine **18** would then experience deprotonation of a distal N-H bond triggering elimination of phosphoric acid and nitrile **19** and leading to aromatization of the heterocyclic core of **1** (Scheme 5) (Fig. 1).

It should be pointed out that in acidic medium, nitrile **19** exists in equilibrium with highly electrophilic protonated form **20** (Scheme 6). We believe that this form might be responsible for the featured *peri*-annulation process according to the mechanism described in Scheme 6. Indeed, nucleophilic attack of the aniline moiety in perimidine **4** should afford amidinium species **21**, which should exist in equilibrium with form **22**. Subsequent 6-*exo-trig* nucleophilic ring closure should provide diaminomethanaminium moiety **23**, that could experience a proton transfer to arrange an *exo*-cyclic ammonium leaving group in structure **24**. Finally, elimination of ammonia would afford cyclic amidinium **25**, which, after deprotonation, would provide 1,8-dihydropyrimido[4,5,6-*gh*]perimidine structure **3** (Scheme 6). The latter would be again oxidized by nitroalkanes



Scheme 6

into TAPy (**1**), as described in Scheme 5, and during this process nitrile **19** would be regenerated.

The following empirical observation strongly supports this mechanistic hypothesis. Firstly, trace amounts of phenylacetonitrile were detected by GC and HRMS in reactions mixtures involving nitroalkane **10d**. Secondly, *peri*-annulation of compound **4b** with acetonitrile (instead of nitroethane) proceeded under similar reaction conditions (inert atmosphere was used to minimize aerobic oxidation) affording mixtures of **3bb** and small amounts of **1bb** (the latter was presumably formed due to oxidation during isolation). Thirdly, this mixture was quickly transformed into pure **1bb** after treatment with nitroethane in 86% PPA.

Having in hand such an efficient protocol for the synthesis of TAPy structures **1** from perimidine precursors **4**, we reserved the efforts to expand this methodology into a double-fold cyclocondensation; simultaneously installing two six-membered heterocyclic rings on the naphthalene-1,4,5,8-tetraamine (**2**). To test this idea we treated a solution of tetraamine **2** in 86% PPA with an excess of nitroalkane (**10a**, **10b**, or **10c**) at 100–150 °C (see Experimental part for details). Gratifyingly, the desired process proceeded smoothly, affording the corresponding symmetric TAPy structures (**1aa**, **1bb**, or **1cc**, respectively) as sole products, although only in medium yields (Scheme 7).

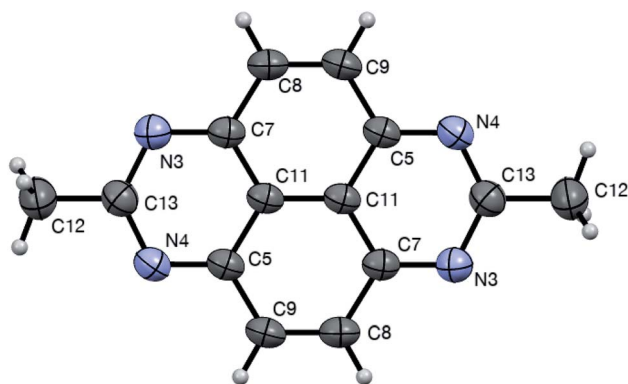
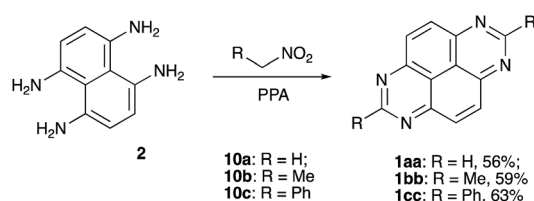


Fig. 1 ORTEP drawing of crystal structure of compound **1bb** (CCDC 1544322†) showing atom numbering labels and 50% probability amplitude displacement ellipsoids.



Scheme 7



## Conclusions

In conclusion, we have developed highly efficient and chemoselective method for the synthesis of tetraazapyrenes (TAPy) based on the reaction of 1*H*-perimidine-6,7-diamines or naphthalene-1,4,5,8-tetraamine with nitroalkanes. This reaction demonstrates a very curious example of PPA-assisted activation of nitroalkane species towards nucleophilic attack. Interestingly, the electrophilically activated nitroalkane also plays a role of mild and efficient oxidant, providing direct access to the TAPy aromatic core and allowing excluding poorly controllable aerobic oxidation step.

## Experimental part

<sup>1</sup>H and <sup>13</sup>C NMR (DEPT-Q) spectra were recorded on a Bruker Avance-III spectrometer (400 or 100 MHz, respectively) equipped with BBO probe in CDCl<sub>3</sub>, using TMS as an internal standard. The abbreviation “ $\psi$ t” is used in listed spectra for doublets of doublets with non-resolved central lines. High-resolution mass spectra were registered with a Bruker Maxis spectrometer (electrospray ionization, in MeCN solution, using HCO<sub>2</sub>Na–HCO<sub>2</sub>H for calibration). Melting points were measured with a Stuart smp30 apparatus. All reactions were performed in oven-dried 5 mL Erlenmeyer flasks (that can be open to the atmosphere), employing overhead stirring. Reaction progress and purity of isolated compounds were monitored by TLC on Silufol UV-254 plates. Perimidines **4a–b** (in the form of trihydrochlorides),<sup>4</sup> hexachlorostannate of tetraaminonaphthalene **2**,<sup>3b</sup> and nitroalkenes **10b**, **c**<sup>13</sup> were prepared according to the literature procedures. All other reagents and solvents were purchased from commercial vendors and used as received.

### General procedure for preparation of 1,3,6,8-tetraazapyrenes from 1*H*-perimidine-6,7-diamines (method A)

Reaction vessels charged with diaminoperimidine trihydrochloride (0.5 mmol), nitroalkane (1.0 mmol), and polyphosphoric acid (86% P<sub>2</sub>O<sub>5</sub>, 1.5 g) were vigorously stirred and heated at appropriate temperature (14 h at 100 °C for reactions involving nitromethane; 3 h at 110 °C for nitroethane, and 8 h 150 °C for phenylnitromethane and phenylnitroethane, respectively). Initially, intense foaming of the mixture was observed, which seized as the process progressed. Upon completion of the reaction, the mixture was poured into cold water (50 mL), neutralized with aqueous ammonia, extracted with ethyl acetate (5 × 70 mL), and concentrated in vacuum. Compounds **1aa**, **1ab**, **1bb** can be obtained in pure form after trituration of the residue in dichloromethane (1 mL) and subsequent filtration. The filtrate was concentrated and purified by flash column chromatography eluting with ethyl acetate to obtain an additional crop of material (about 15–20%). For all other compounds, combined ethyl acetate extracts were concentrated and the residual material was purified by preparative column chromatography on silica gel eluting with ethyl acetate.

### General procedure for preparation of 1,3,6,8-tetraazapyrenes from naphthalene-1,4,5,8-tetraamine (method B)

This protocol is identical to the one described above (method A), except for employing a mixture of naphthalene-1,4,5,8-tetraamine **2** (in the form of the stable hexachlorostannate that can be taken directly from reduction of the corresponding nitroarenes)<sup>3b,14</sup> (0.261 g, 0.5 mmol), nitroalkane (2.0 mmol), and polyphosphoric acid (86% P<sub>2</sub>O<sub>5</sub>, 2.5 g).

### Pyrimido[4,5,6-*gh*]perimidine (**1aa**)<sup>10,15</sup>

This material was obtained as a yellowish crystalline solid, mp over 300 °C, *R*<sub>f</sub> 0.15 (10% EtOH/EtOAc); yield 65 mg (0.32 mmol, 63%) – *via* method A; 58 mg (0.28 mmol, 56%) – *via* method B; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ , ppm: 10.08 (s, 2H), 8.71 (s, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ , ppm: 158.0 (2C), 152.8 (4C), 136.5 (4C), 114.2 (2C); IR (NaCl, cm<sup>−1</sup>): 3050, 1603, 1437, 1240, 1180, 965, 843, 712; HRMS (ES TOF) calcd for C<sub>12</sub>H<sub>7</sub>N<sub>4</sub> (M + H)<sup>+</sup>: 207.0665, found 207.0660 (2.4 ppm).

### 2-Methylpyrimido[4,5,6-*gh*]perimidine (**1ab**)<sup>10</sup>

This material was obtained as a yellowish crystalline solid, mp over 300 °C, *R*<sub>f</sub> 0.21 (10% EtOH/EtOAc); yield 79 mg (0.36 mmol, 72%) – *via* method A in reaction of **4a** with **10b**; 69 mg (0.32 mmol, 63%) – in reaction of **4b** with **10a**; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ , ppm: 9.92 (s, 1H), 8.51 (d, *J* = 9.5 Hz, 2H), 8.45 (d, *J* = 9.5 Hz, 2H), 3.17 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ , ppm: 168.6, 155.8, 154.7 (2C), 152.4 (2C), 137.1 (2C), 135.2 (2C), 113.7 (2C), 25.3; IR (NaCl, cm<sup>−1</sup>): 3057, 1562, 1551, 1478, 1491, 1355, 1342, 856; HRMS (ES TOF) calcd for C<sub>13</sub>H<sub>9</sub>N<sub>4</sub> (M + H)<sup>+</sup>: 221.0822, found 221.0825 (1.4 ppm).

### 2,7-Dimethylpyrimido[4,5,6-*gh*]perimidine (**1bb**)<sup>11b</sup>

This material was obtained as a yellowish crystalline solid, mp over 300 °C, *R*<sub>f</sub> 0.25 (10% EtOH/EtOAc); yield 91 mg (0.39 mmol, 78%) – *via* method A; 69 mg (0.30 mmol, 59%) – *via* method B; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ , ppm: 8.35 (s, 4H), 3.03 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ , ppm: 166.9 (2C), 152.3 (4C), 135.6 (4C), 111.6 (2C), 26.8 (2C); IR (NaCl, cm<sup>−1</sup>): 3055, 1569, 1558, 1493, 1485, 1361, 1347, 858; HRMS (ES TOF) calcd for C<sub>14</sub>H<sub>11</sub>N<sub>4</sub> (M + H)<sup>+</sup>: 235.0978, found 235.0983 (2.1 ppm).

### 2-Phenylpyrimido[4,5,6-*gh*]perimidine (**1ac**)<sup>11a</sup>

This material was obtained as a yellowish crystalline solid, mp over 300 °C, *R*<sub>f</sub> 0.63 (10% EtOH/EtOAc); yield 102 mg (0.36 mmol, 72%) – *via* method A in reaction of **4c** with **10a**; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ , ppm: 9.66 (s, 2H), 8.81 (d, *J* = 8.3 Hz, 2H), 8.57 (d, *J* = 9.5 Hz, 2H), 8.52 (d, *J* = 9.5 Hz, 2H), 7.64–7.59 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ , ppm: 165.9, 155.4, 154.7 (2C), 152.4 (2C), 138.4, 137.2 (2C), 135.2 (2C), 133.0, 131.2 (2C), 129.3 (2C), 114.2, 112.7; FT IR (NaCl, cm<sup>−1</sup>): 3052, 1577, 1555, 1499, 1483, 861, 723, 641; HRMS (ES TOF) calcd for C<sub>18</sub>H<sub>11</sub>N<sub>4</sub> (M + H)<sup>+</sup>: 283.0978, found 283.0971 (2.5 ppm).





## 2-Methyl-7-phenylpyrimido[4,5,6-*gh*]perimidine (1bc)<sup>11b</sup>

This material was obtained as a yellowish crystalline solid, mp over 300 °C, *R<sub>f</sub>* 0.75 (10% EtOH/EtOAc); yield 105 mg (0.36 mmol, 71%) – *via* method A in reaction of **4b** with **10c**; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm: 8.84 (d, *J* = 8.3 Hz, 2H), 8.66 (d, *J* = 9.5 Hz, 2H), 8.56 (d, *J* = 9.5 Hz, 2H), 7.61 (ψt, 1H), 7.55 (d, *J* = 7.4 Hz, 2H), 3.24 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ, ppm: 166.8, 164.0, 153.0 (4C), 138.4, 136.8 (2C), 135.9 (2C), 133.0, 131.3 (2C), 129.2 (2C), 112.8 (2C), 21.2; FT IR (NaCl, cm<sup>-1</sup>): 3036, 1579, 1554, 1491, 1482, 858, 775, 637; HRMS (ES TOF) calcd for C<sub>19</sub>H<sub>13</sub>N<sub>4</sub> (M + H)<sup>+</sup>: 297.1135, found 297.1129 (2.0 ppm).

## 2,7-Diphenylpyrimido[4,5,6-*gh*]perimidine (1cc)<sup>11b</sup>

This material was obtained as a yellowish crystalline solid, mp over 300 °C, *R<sub>f</sub>* 0.85 (10% EtOH/EtOAc); yield 113 mg (0.32 mmol, 63%) – *via* method B; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm: 8.84 (d, *J* = 8.5 Hz, 4H), 8.68 (s, 4H), 7.63–7.52 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ, ppm: 167.0 (2C), 152.3 (4C), 139.1 (2C), 135.2 (4C), 133.1 (2C), 131.3 (4C), 129.5 (4C), 113.0 (2C); FT IR (NaCl, cm<sup>-1</sup>): 3045, 1573, 1561, 1499, 1485, 852, 770, 641; HRMS (ES TOF) calcd for C<sub>24</sub>H<sub>15</sub>N<sub>4</sub> (M + H)<sup>+</sup>: 359.1291, found 359.1301 (2.8 ppm).

## 2-Benzylpyrimido[4,5,6-*gh*]perimidine (1ad)

This material was obtained as a yellowish crystalline solid, mp over 300 °C, *R<sub>f</sub>* 0.65 (10% EtOH/EtOAc); yield 93 mg (0.32 mmol, 63%) – *via* method A in reaction of **4a** with **10d**; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm: 10.01 (s, 1H), 8.51 (d, *J* = 9.9 Hz, 2H), 8.47 (d, *J* = 9.9 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.35–7.32 (m, 2H), 7.21, 7.23–7.19 (m, 1H), 4.23 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ, ppm: 163.2, 157.9, 152.3 (2C), 151.6 (2C), 139.7, 136.4 (2C), 134.5 (2C), 129.4 (2C), 128.6 (2C), 126.7, 115.2 (2C), 29.8; FT IR (NaCl, cm<sup>-1</sup>): 3047, 1582, 1555, 1491, 1475, 863, 761, 633; HRMS (ES TOF) calcd for C<sub>19</sub>H<sub>13</sub>N<sub>4</sub> (M + H)<sup>+</sup>: 297.1135, found 297.1143 (2.7 ppm).

## 2-Benzyl-7-methylpyrimido[4,5,6-*gh*]perimidine (1bd)

This material was obtained as a yellowish crystalline solid, mp over 300 °C, *R<sub>f</sub>* 0.76 (10% EtOH/EtOAc); yield 102 mg (0.33 mmol, 66%) – *via* method A in reaction of **4b** with **10d**; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm: 8.53 (s, 4H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.35–7.32 (m, 2H), 7.21, 7.23–7.19 (m, 1H), 4.18 (s, 2H), 3.19 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ, ppm: 166.8 (2C), 152.1 (4C), 137.7, 135.4 (4C), 129.0 (2C), 128.2 (2C), 126.6, 111.4 (2C), 29.2, 26.6; FT IR (NaCl, cm<sup>-1</sup>): 3053, 1574, 1568, 1483, 1489, 1351, 1344, 866; HRMS calcd for C<sub>20</sub>H<sub>15</sub>N<sub>4</sub> (M + H)<sup>+</sup>: 311.1291, found 311.1282 (2.9 ppm).

## Reaction of **4b** with acetonitrile to intercept 2,7-dimethyl-1,8-dihydropyrimido[4,5,6-*gh*]perimidine (**3bb**) (method C)

A mixture of 2-methyl-6,7-diaminoperimidine trihydrochloride (71 mg, 0.25 mmol) and polyphosphoric acid (86% P<sub>2</sub>O<sub>5</sub>, 1.0 g) was vigorously stirred under argon atmosphere and dry acetonitrile (52 μL, 41 mg, 1.0 mmol) was injected in a single portion. The mixture was heated for 3 h at 100 °C, and then poured into freshly distilled degassed water (50 mL), neutralized with

aqueous ammonia, extracted with EtOAc (5 × 50 mL), and concentrated under argon. Crude compound **3b** was isolated as brownish-red solid, *R<sub>f</sub>* 0.10 (EtOAc/EtOH 8 : 1), relatively stable in solid form stored under inert atmosphere, but quickly decomposing in solutions or upon contact with air. GC detection as well as mass-spectral characterization of this compound proved impossible due to very rapid oxidation into **1bb** upon heating. Our attempt to measure of <sup>13</sup>C NMR spectrum also proved unfruitful, since this compound decomposes in solutions faster than it was necessary to accumulate sufficient number of scans for carbon spectrum. We were able to measure <sup>1</sup>H NMR spectrum (see ESI† for spectral chart). This experiment demonstrated, that **3bb** exists in solution in CDCl<sub>3</sub> as a mixture of equilibrating 1,8-dihydro- and 1,6-dihydro-tautomers along with minute amount of oxidized product **1bb**.

## Reaction of 2,7-dimethyl-1,8-dihydropyrimido[4,5,6-*gh*]perimidine (**3bb**) with nitroethane in PPA

Compound **3bb** (59 mg, 0.25 mmol) obtained in the reaction of **4b** and acetonitrile as described above (method C) was stirred at 100 °C in 86% PPA (1.0 g) under argon atmosphere. Nitroethane (18 μL, 19 mg, 0.25 mmol, 1.00 equiv.) was injected in a single portion and the stirring was continued for 3 min, after which color of the reaction mixture changes from dark-red to green indicating the completion of the oxidation process. The post-reaction work up and isolation of the product was carried out in the same way as described for method A. Compound **1bb** (47 mg, 0.20 mmol, 80%) was obtained as sole product. Physical and spectral properties of this material were identical to those described above for the sample obtained *via* method A.

## Acknowledgements

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## Notes and references

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