

Straightforward, Sustainable and Scalable Access to 3,4-Perylenedicarboxylic Monoanhydride

Anita Zucchi, Sara Mattiello, Mauro Sassi,* and Luca Beverina

*Department of Materials Science, University of Milano-Bicocca, Via R. Cozzi, 55, Milano,
Italy. I-20125*

E-mail: mauro.sassi@unimib.it

Phone: +39 02 6448 5194

Abstract

Perylene dyes are a cornerstone of modern research and technology in fields ranging from printed (opto)electronics to bioimaging. Most known compounds are bisimide derivatives prepared from perylenetetracarboxylic dianhydride (PTCDA), essentially a chemical commodity. On the contrary, there are comparatively fewer reports on perilenedicarboxylic monoimide derivatives not due to lack of performance but due to the challenging access to the key intermediate 3,4-perylenedicarboxylic monoanhydride (PDCMA). As we detail, reported synthetic pathways are both costly, resource intensive and associated with extremely poor green metrics. We show a new two-step straightforward, sustainable, efficient and organic solvent free preparation of PDCMA based on a combination of solventless and in-water reactions.

Keywords

perylene monoanhydride, perylene dyes, scalable synthesis, green chemistry

Synopsis

A new sustainable two-step high yield synthesis of the key perylene dye intermediate 3,4-Perylenedicarboxylic Monoanhydride is reported and compared to existing protocols using green metrics.

Introduction

Perylene dyes documented applications cover most if not all technologies requiring conjugated molecular and polymeric materials. Over the last few decades, leading research groups developed functionalized perylene derivatives with state-of-the-art applications in research fields as diverse as organic transistors, theranostic platforms,¹ imaging and bioimaging² and photovoltaic technologies.³ Of all perylene dyes related structures, perylenediimides (PDIs) get the lion's share.⁴ This is without doubt because of their performances, but also due to wide availability of their common precursor perylenetetracarboxylic dianhydride (PTCDA), a chemical commodity. PDIs are planar, rigid, and symmetric structures featuring characteristic spectral signatures: efficient and vibronically resolved absorption and emission profiles, very limited Stokes shift and no net dipole moment. Such features make them ideal for most but not all applications. They lack the directional charge transfer excitation and high Stokes shifts required for example in photocatalysis, solar technologies and bioimaging. Perylenemonoimides (PMIs) – the non-symmetric equivalent of PDIs – combine the typical features of PDIs with the additional characteristics of Donor-Acceptor compounds.⁵ Despite the somewhat complementary nature of PDIs and PMIs, literature reports 5800 distinct PDIs derivatives described in over 10000 papers and only 293 PMIs dyes in 334 papers. Such striking overrepresentation of PDIs does not exclusively stem from performances but is also the consequence of a more synthetically challenging preparation. Perylenedicarboxylic monoanhydride PDCMA is the gatekeeper to the PMIs class. Unlike PTCDA, it is not commercially available and somewhat difficult to make, especially on a large scale. The vast

majority of the existing synthetic approaches rely on a defunctionalization strategy starting from PTCDA and aiming at an overall selective and efficient hydrodecarboxylation with removal of one of the two anhydride functional groups. Although a one pot direct procedure for this transformation can theoretically be conceived, the only successful implementation was reported by Langhals et al. by treatment of PTCDA at 170 °C in a steel autoclave with a non-condensing tertiary amine (Hünig's base) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in imidazole (Scheme 1, route A).⁶ While advantageous in reducing the number of reaction steps and derivatizations, the method has a modest 24% yield and requires a lengthy and hardly scalable purification procedure involving saponification into the poorly water soluble potassium salt, chloroform extraction to remove byproducts, reacidification, filtration and additional extensive washing of the solid product. Although not particularly efficient, this direct approach is still competitive with the two-step procedure originally proposed by Langhals himself (Scheme 1 route B).^{7,8} According to such protocol, PTCDA undergoes a decarboxylative imidation by reaction with 2,5-ditertbutylaniline in the presence of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ as catalyst and in imidazole/water as the solvent. The reaction again requires the use of a pressurized steel vessel and prolonged heating at 190 °C for nearly one day. A crude mixture containing unreacted PTCDA, target **1** and side products (perylene and the corresponding symmetric perylenebisimide) is obtained. The isolation of pure **1** from such a complex mixture requires a solvent, silica and time-consuming chromatography due to the relatively poor solubility of **1** combined with the presence of the insoluble PTCDA. Monoimide **1** can then be converted into the target PDCMA by hydrolysis with KOH in ^tBuOH, followed by acidification. The overall yield can vary depending on the details of the specific preparation but does not exceed 35% and the scale of the reaction is limited both by the need for an autoclave and by the low solubility and aggregation behavior of **1**, impacting on chromatography.

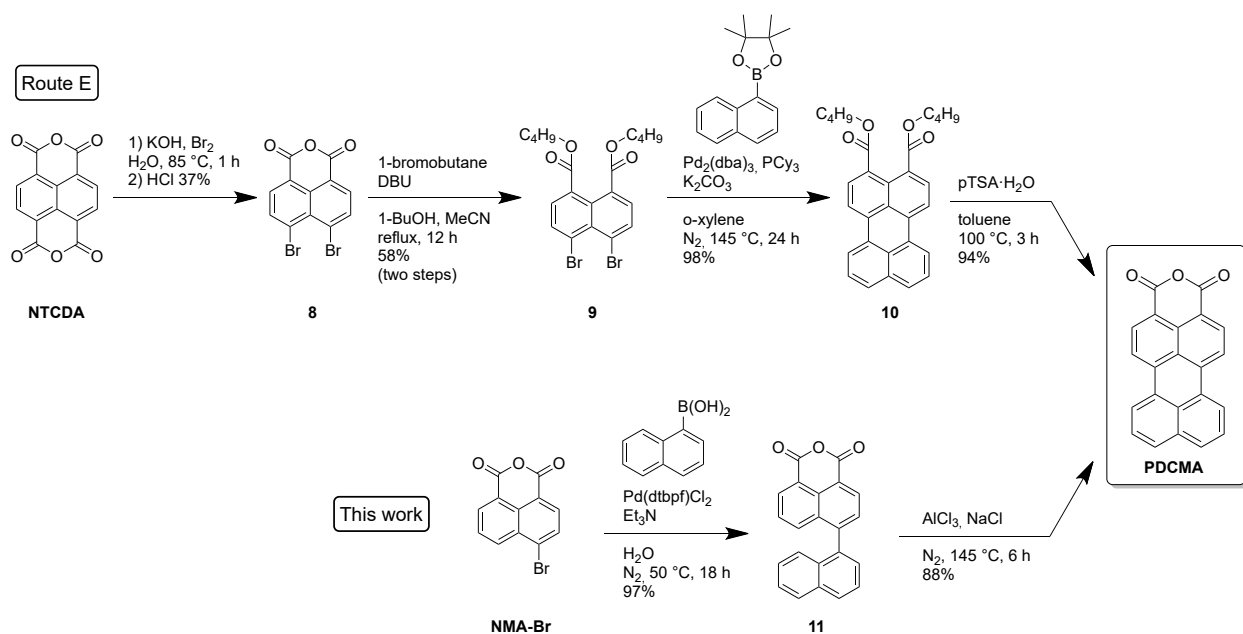
Nagao et al. earlier developed a closely related approach to 3,4-perylenedicarboxylic acid derivatives (route C) requiring partial saponification of PTCDA with KOH to give potassium salt **2**, followed by condensation with one equivalent of an aliphatic amine, enabling

the selective precipitation of the monoimide-monoanhydride derivative **3**.⁹ The latter is hydrodecarboxylated in the presence of KOH 12% under pressure at high temperature to give the monoimide **4**.¹⁰ Unfortunately, they did not report on the hydrolysis of **4** to PDCMA.

Such void is at least partially filled by the results of Wasielewski et al. who performed such hydrolysis on the isomeric N-(2-ethylhexyl) perylene monoimide (55% yield).¹¹ Taking this data into account, such tortuous 4-step route is expected to provide an overall 34% yield of PDCMA avoiding chromatography and making use of benign solvents (water and alcohols), although it still requires an high pressure/high temperature reaction step that limits scalability.

Recently, Xiao et al. described a different 4-step method that is worth mentioning as it is reasonably efficient, and suitable for scaling up (route D).¹² In the first step, PTCDA is quantitatively converted in the corresponding tetraester **5** by reaction with 1-bromodecane in the presence of tetraoctylammonium bromide, NaOH and KI. The latter is partially hydrolyzed and closed to the diester monoanhydride **6** by reaction with stoichiometric pTSA monohydrate, in good 74% yield. A bronze promoted decarboxylation in 3-picoline gives diester **7** in 87% yield after purification by column chromatography. pTSA monohydrate promoted acid hydrolysis gives PDCMA directly in 97% without the need for further purification. All such defunctionalization protocols have plus and minuses (see also Section 3 of ESI), with route D multistep protocol being preferable as it was performed on the largest reported scale to date (~3 g of PDCMA) and does not require the use of high pressure vessels.

An entirely different approach directly targets the final PDCMA synthesizing the perylene core starting from two naphthalene based building blocks through coupling and cyclization. The application of this strategy was introduced by Würtner et al.¹³ for the synthesis of a 3,4-perylenemonoimide derivative and recently extended by Stupp et al. to PDCMA.¹⁴ In this case, as depicted in Scheme 2 naphthalenetetracarboxylic dianhydride (NTCDA) is converted in the dibromide **8** by reaction with Br₂ under alkaline conditions (Hunsdiecker



Scheme 2: PTCDA construction routes as described in the literature (route E), and in this work.

reaction).¹⁵ The reaction requires some caution, particularly on a large scale, due to the large amount of gas evolved. Crude derivative **8** is then esterified to **9** with an overall 58% yield after chromatographic purification. A subsequent cascade Suzuki-Miyaura/arylation with 1-naphthalenboronic pinacol ester with Pd₂dba₃/PCy₃ catalyst in *o*-xylene at 145 °C leads to **7** in 98% yield after chromatographic purification. As already discussed for route D, **7** is then easily hydrolyzed to PDCMA with pTSA (94% yield). The overall 53% multi-step yield is quite remarkable even if it still involves 4 synthetic steps and two chromatographic purifications.

Inspired by this strategy, we here disclose a new access to PDCMA that bypasses the troublesome PTCDA defunctionalization way, but that is also scalable and more sustainable: it requires a much lower amount of processing solvents and does not require the use of autoclave nor chromatography. In doing so, we also quantitatively compare it in terms of efficiency and sustainability with respect to the methods we highlighted above, and provide direct proof of scalability by performing a 10 g scale PDCMA preparation using standard laboratory equipment.

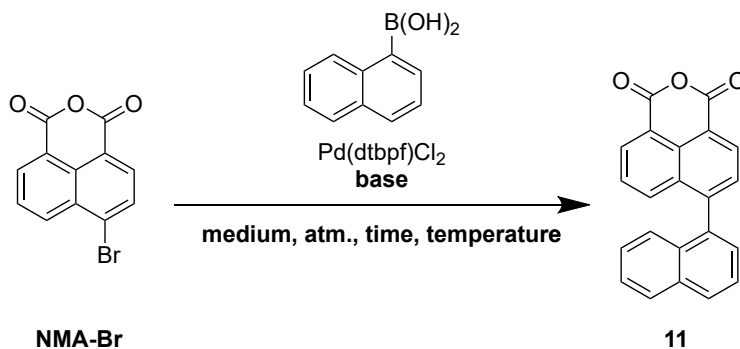
Results and Discussion

Our method uses 4-bromo-1,8-naphthaleneanhydride (NMA-Br) as the starting material. As it is thoroughly discussed in section 2 of SI, NMA-Br is a commodity chemical that can be obtained starting from acenaphthene – the same starting material as PTCDA – in two simple steps.

Individual Step Assessment

Step 1: Suzuki coupling of NMA-Br with 1-naphthaleneboronic acid The first step in our protocol is the potentially troublesome Suzuki-Miyaura coupling of 1-naphthaleneboronic acid with the poorly soluble NMA-Br. We profited from the solubility of the latter in water in the presence of bases in the form of dicarboxylate salt and decided to carry out the reaction directly in water. Indeed, the reaction works smoothly using Et₃N as the base, in slight excess with respect to the ideal stoichiometry. We observed that the extra amount of base was needed to improve the homogeneity of the reaction mixture (table 1, entry 1). We also tested the coupling under micellar catalysis conditions, using Kolliphor EL as the surfactant. In doing so, we did not expect to improve on the yield but aimed at making the reaction easier to handle as the use of such surfactant enables carrying out Pd mediated reactions without the need for deoxygenating the solvent.¹⁶ Unfortunately, none of the conditions we tested (including a partial change in the base from Et₃N to KOH) gave useful results (table 1, entry 2-5), and we proceeded with the scaling up under entry 1 conditions. The 70-fold increase in the scale of the reaction required some further optimization. Gentle heating at 50 °C and overhead stirring helped maintaining the dispersion of reagents and product homogeneous at all times. Under such conditions, reaction reproducibly afforded quantitative conversion of NMA-Br in 18 hours and with 1 mol% Pd(dtbpf)Cl₂ (entry 6). The product was isolated by filtration in 96.7% yield after acidification with a 35% solution of H₂SO₄, and washing with MeOH and Et₂O to remove binaphthyl traces.

Table 1: Suzuki-Miyaura reaction performed in different conditions. Yields were estimated by NMR of crude product.



Trial	Medium	Base (eq.)	Cat. amount (mol%)	Atm.	T (°C)	Time (h)	Yield (%)
1	H ₂ O	Et ₃ N (3.7)	0.02	N ₂	rt	24	97
2	2 wt% K-EL in H ₂ O	Et ₃ N (7.5)	0.02	air	rt	24	44
3	2 wt% K-EL in H ₂ O	KOH (2) Et ₃ N (2.2)	0.02	air	rt	24	-
4	2 wt% K-EL in H ₂ O	KOH (2) Et ₃ N (2.2)	0.02	air	45	24	-
5	2 wt% K-EL in H ₂ O	KOH (2) Et ₃ N (7.1)	0.02	air	45	24	-
6 ^a	H ₂ O	Et ₃ N (3.7)	0.01	N ₂	50	18	96.7

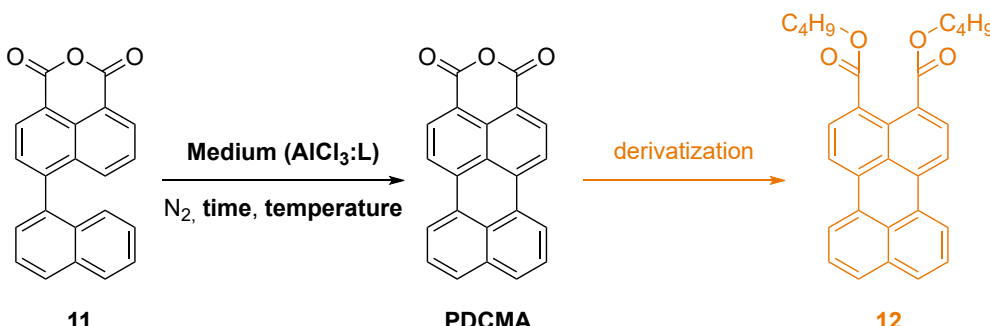
^a Reaction performed with 26.5 g of NMA-Br. The yield refers to the isolated pure product.

Step 2: Cyclization of binaphthyl derivative **11 to PDCMA** This step was performed using a Scholl dehydrogenative cyclization, a vintage Lewis acid promoted arylation method revived in the 2000s by the work of Müllen on hexabenzocoronenes and related derivatives.^{17,18} In 1910 Scholl, after whom the reaction is named, reported the very first synthesis of perylene upon heating 1,1'-binaphthyl in AlCl₃ at 140 °C (albeit in a very low 15% yield).¹⁹ Despite the rather unique feature of allowing aryl-aryl coupling of completely unfunctionalized aromatics and without resorting to expensive transition metal catalyst, the Scholl reaction failed to become a popular method in organic synthesis due to its unreliability and lack of generality. It is more profitably employed with electron rich derivatives, where the use of unreactive solvents and moderate heating affords the products in high yield or whenever the characteristics of the reagents and the product minimize possible side reactions: oligomerizations,²⁰ isomerizations and rearrangements.^{21,22} As expected, the application of the Scholl reaction on an electron-poor derivative such as **11** required extensive optimization to find the best conditions to achieve the desired PDCMA with optimal yield and selectivity. Aiming at the development of a sustainable method, we discarded organic solvents. We tested the direct reaction of neat **11** with excess AlCl₃ (the original Scholl conditions) as well as two different kinds of chloroaluminate based lewis acidic ionic solvents: a) AlCl₃:NaCl molten salts with a composition corresponding or close to the eutectic point and b) AlCl₃:trimethylammonium chloride (TMAHCl) lewis acidic ionic liquid. Both mixtures are liquids at the reaction temperature, which helps in achieving a homogeneous (blue colored) reaction mixture. In all cases, we monitored the disappearance of the precursor by TLC inspection, observing a faster conversion for ionic solvents reactions with respect to pure AlCl₃. Pouring of the reaction mixture in 5 wt% HCl results in the formation of a dark red precipitate that can be isolated by suction filtration. Prolonged washing of this precipitate with EtOH in a Soxhlet extractor is able to remove all inorganic impurities as assessed by TGA in air (see SI). The purity of the resulting PDCMA is strongly dependent on the reaction conditions and its assay is crucial to probe the reaction efficiency.

This task is complicated by the extremely poor solubility of the product and the possible byproducts formed under unoptimized conditions. The latter result from rearrangement (*ie.* benzo[k]fluoranthene, benzo[j]fluoranthene derivatives), complete or partial decarboxylation (*ie.* perylenecarboxylic acid, perylene), oligomerization (*ie.* terrylene derivatives or higher rylenes) or from a combination of such mechanisms.

We thus developed a derivatization procedure leading to the formation of a soluble PDCMA derivative (ester **7**, Scheme 2) that could be isolated by chromatography and thoroughly characterized. The esterification of an analytical PDCMA sample with 1-bromobutane in BuOH in the presence of KOH and tetrabutylammonium bromide (TBAB) gives ester **7** in essentially quantitative yield. We repeated such esterification under identical conditions with fixed aliquots of crude PDCMA and we used the isolated amount of **7** as a gauge of the effective yield and purity of starting material. Table 2 summarizes the results we obtained.

Table 2: Scholl reaction performed in different reaction medium. All reactions performed with 2 g of precursor **11**, unless otherwise specified. Yields were estimated by esterification of crude product to pure **10** (derivatization step).



Trial	Medium	Composition (mol%)	AlCl ₃ eq.	T (°C)	Time (h)	Crude yield (wt. %)	PDCMA yield (%)
1	AlCl ₃	–	5	140	24	79	58
2	AlCl ₃ :NaCl	61:39	5	145	24	82	42
3	AlCl ₃ :NaCl	69:31	12	150	7	92	60
4	AlCl ₃ :NaCl	69:31	61	150	7	88	88
5	AlCl ₃ :TMAHCl	67:33	68	80	8	77	29
6 ^a	AlCl ₃ :NaCl	69:31	61	150	4	86	86

^a Reaction performed with 10 g of reagent **11**.

Performing the reaction in neat AlCl_3 is possible but unpractical (entry 1), particularly when scaling up. Precursor **11** mixes readily with AlCl_3 but the reaction mixture quickly turns into a dark sticky residue that is difficult to stir efficiently. Operating above 140°C to improve mixing is not helpful as it promotes decarboxylation with the formation of perylene, especially for longer reaction times. While the mass recovery is 79% (derivative **11** and PDCMA have essentially the same molecular weight), a relatively modest 58% combined yield of pure **7** was obtained. Most of the impurities formed likely consists of the aforementioned oligomerization byproducts as testified by the presence of dark colored and insoluble species not eluting during chromatography. The use of molten salts enables the reaction to be carried out under homogeneous conditions, with obvious advantages in mixing as well as better reaction temperature control. We first tested the AlCl_3 : NaCl eutectic mixture (a liquid above 130°C)²³ using the same AlCl_3 /**11** ratio we employed for the neat reaction. Although we obtained a slightly higher mass recovery (Table 2, entry 2, 82%), the crude PDCMA had a lower purity, as the more modest 42% combined yield of **7** testifies. The performances improved significantly by increasing the amount of Lewis acidic ionic solvent (equivalent to a 12-fold AlCl_3 excess) and employing an higher AlCl_3 molar fraction (69 mol%). These conditions enabled a shortening of the reaction time to 7 h and improved mass recovery to 92% (entry 3). This higher reactivity is consistent with speciation equilibrium in chloroaluminate-based molten salts where Lewis acidity varies according to the increase in the concentration of Al_2Cl_7^- upon the increase of the AlCl_3 molar fraction. Mechanistically this is explained by the fact that the dimeric Al_2Cl_7^- features an easily broken chloride bridge and can thus react with a Lewis base (our substrate) according to the equation: $\text{Al}_2\text{Cl}_7^- + \text{L} \longrightarrow \text{AlCl}_4^- + \text{AlCl}_3 \leftarrow \text{L}$.^{24,25} The latter is the σ -complex that leads to the active arenium cation in the Scholl mechanism.^{21,26} Despite such improved reactivity, the purity of the crude was still unsatisfactory as the yield assessed through esterification remained a modest 60%. A further increase of the molten salt excess did not significantly impact on recovery (88%) but gave essentially quantitative yield in the esterification reaction (entry

4), thus vouching for a very high purity of the Scholl product obtained under such conditions. We speculate that this might be the result of the higher dilution favoring the desired intramolecular reaction over possible intermolecular side processes leading to the formation of insoluble oligomers. The use of $\text{AlCl}_3\cdot\text{TMAHCl}$ (Table 2 entry 5), a still reasonably cheap and easier to handle alternative chloroaluminate based Lewis acidic ionic liquid, allowed to test the reaction at a lower temperature (80°C), leading to a similar mass recovery (77%) but a dramatically poorer esterification yield (29% estimated yield of PDCMA). We thus did not further investigate mixtures containing ammonium salts and proceeded with scaling up. Entry 4 reaction can be scaled up to 10 g of precursor **11** with consistent mass recovery and purity, leading to the preparation of 8.8 g of pure PCDMA in a single batch (entry 6). None of the so far described synthesis of PDCMA could achieve such a scale in a single preparation and without the need for chromatography.

Finally, we also take our best effort to attain a complete and accurate NMR characterization of PCDMA prepared under our optimized conditions. PDCMA and possible byproducts have very low solubility in all common solvents including CDCl_3 , the solvent used to acquire the only reported ^1H NMR spectrum.¹¹ This limits the ability to detect the presence of such impurities because of the limits in sensitivity of routine NMR experiments. Therefore, we tested pyridine- d_5 , obtaining improved results. Further trials finally lead us to select a $\text{CDCl}_3\text{:CF}_3\text{COOD}$ 60:40 wt% mixture which provided good solvency enabling the acquisition of NMR spectra (including the previously unreported ^{13}C spectrum) with good resolution and S/N ratio.²⁷

Reaction Pathway Greenness Evaluation and Benchmarking

Our method is not only more efficient and scalable, but also significantly more sustainable. Figure 1 compares the E-factor (the weight ratio between wastes and product of the whole process), the number and type of unitary operations, and the overall yield of our procedure with respect to the routes described previously in the literature. We also included an estimate

of the cost of raw materials per g, based on retail prices on a laboratory scale.

From the point of view of efficiency, as measured by overall yield, the herein proposed method proved to be the best performing one (85%) followed by the 4-steps routes D (57%) and E (53%). Regarding the evaluation of greenness, all existing procedures proved underperforming from the point of view of sustainability as evaluated by their E-factors and associated hazards (2). In this respect, route B (4300), D (4100) and E (3880) are mostly plagued by the presence of chromatographic purification steps that require ample amount of silica and chlorinated solvents. Nonetheless, even when the impact of chromatography is completely absent (routes A and C), the low solubility of intermediates leads to a remarkably high consumption of processing solvents whenever liquid-liquid extractions or simple solubilization of intermediates is required. This aspect is clearly testified by the poor performance of route A (3360), and C (3970). In comparison, the herein proposed route provides a far better result with an E-factor of 240 thanks to the low amount of solvents required. Aiming at sustainability, the order of magnitude reduction in the E-factor is particularly relevant, as PDCMA is an intermediate rather than an active compound.

Figure 2 gives a breakdown of the E-factor of the different routes, giving information on the specific hazards of the employed raw materials. The graph reports the mass of raw material required per unit mass of product, indexed for the corresponding GHS pictogram. Our route is advantageous in all comparisons, with particular emphasis on the absence of chemicals having acute toxicity and posing environmental threats. In addition, the aluminum containing aqueous waste produced, can be easily recycled by simple controlled basification with NaOH leading to nanocrystalline boehmite (γ -AlO(OH)) that can be further converted in γ -Al₂O₃ by calcination according to established procedures.²⁸

Finally, product costs, estimated solely from the costs of the chemicals involved in the process, follow a closely related pattern as the large part of them can be ascribed to processing solvents. Values fall within the range from 42.1 €/g (for the 4-step route D) to 17.6 €/g (for the one-step route A). Here again, the proposed route proves to be an outlier with an

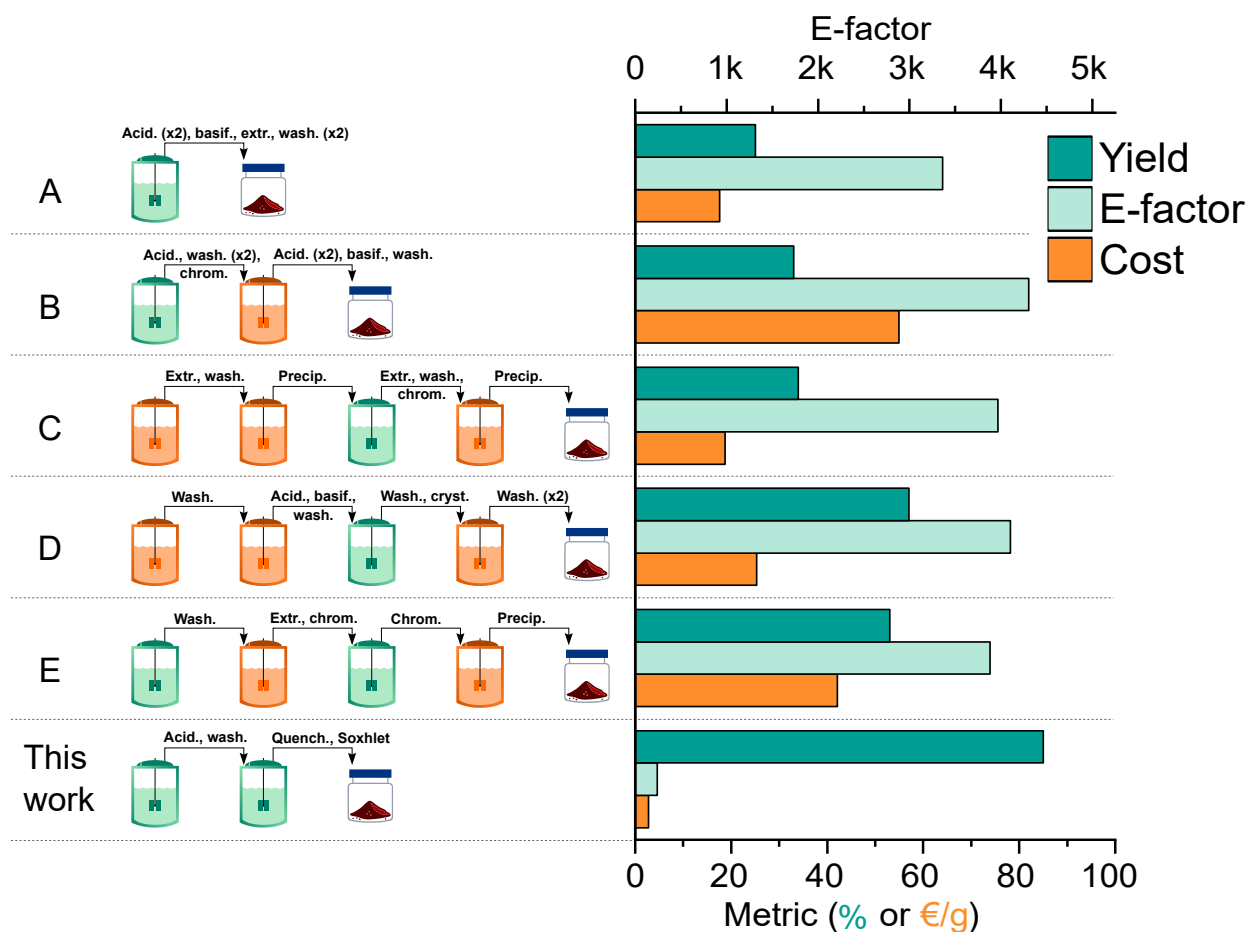


Figure 1: Comparison of sustainability, efficiency, and cost of all the reported routes for the preparation of PDCMA. On the left: schematic representation of the synthetic paths, and the unitary operations needed for product purification at each step (the green and orange reactors symbolize construction steps and concession steps, respectively). On the right: estimate of E-factor, cost and yield of every procedure.

estimated cost of only 2.8 €/g.

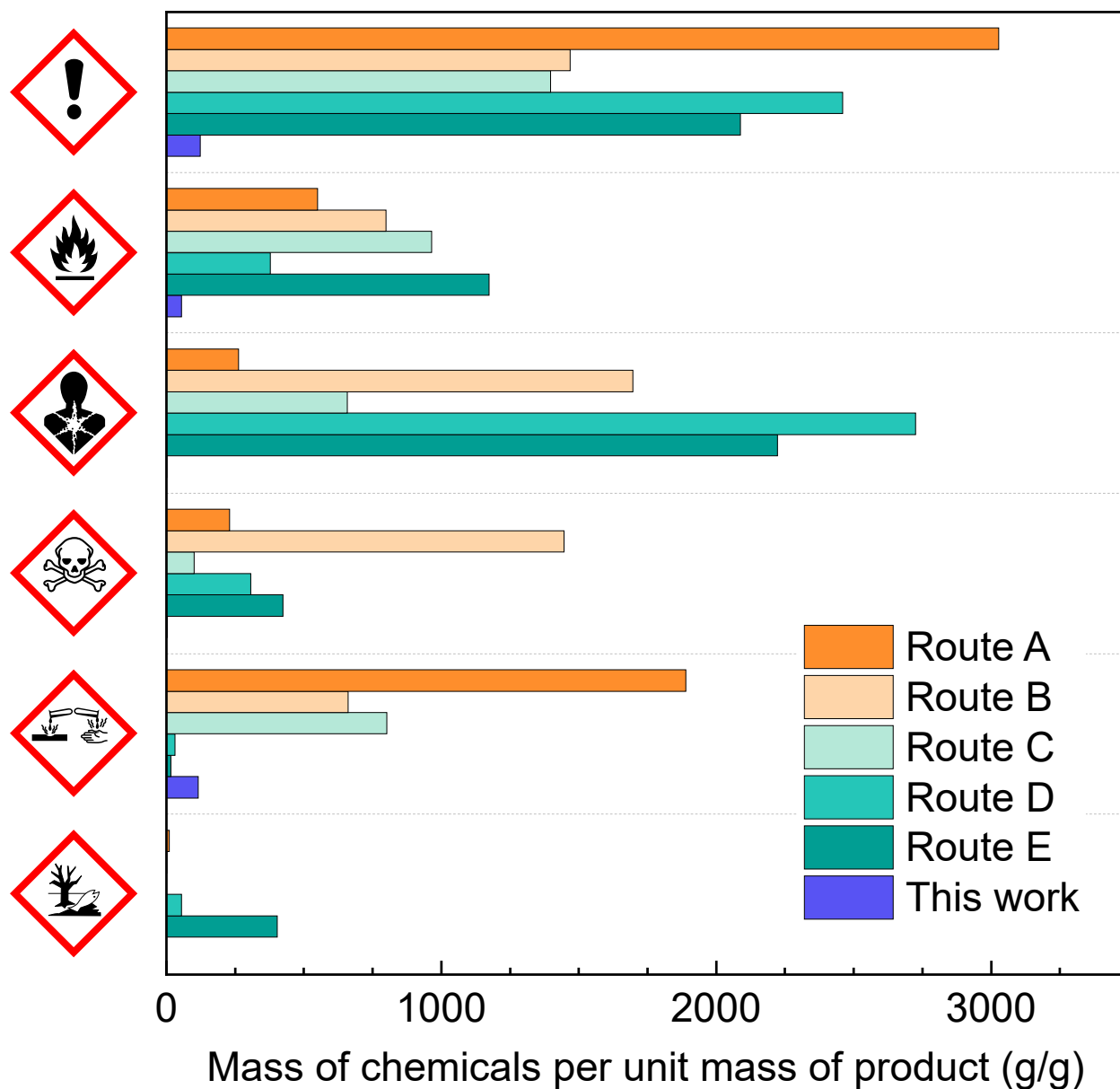


Figure 2: Comparison of the mass of raw materials per unit mass of product as a function of the corresponding Hazard Class Pictograms for all the reported syntheses of PDCMA

Conclusions

In conclusion, we have developed a facile, two-step high yield synthesis of PDCMA, the crucial intermediate for the preparation of the whole class of PMIs materials. Our route

is advantageous with respect to those previously published not solely in terms of efficiency and cost, but also greener as assessed by the reduced E-factor and the reduction of hazards associated with raw materials and waste. We foresee this to provide a positive effect on the overall environmental impact of PMIs-based technologies, and to open the path toward the preparation of perylene 3,4-diesters and their derivatives, which, at the moment, are essentially absent in the scenario. Relevant for industrial applications are the ease of scaling up and the absence of chlorinated solvents during all the synthetic and purification steps.

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Supporting Information Available

The Supporting Information are available free of charge.

- Materials and methods for the preparation of PDCMA, **11** and **10**. Details on calculation of green metrics employed and of cost model selected. Details on calculations of cost and E-factor according to literature data. Details on calculation of E-Factor and cost according to the procedure described in this paper. TGA characterization of PDCMA. Copies of ^1H and ^{13}C NMR spectra of all compounds.

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TOC Graphic

