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Dipyreno- and diperyleno-anthracenes from glyoxylic Perkin reactions[†]

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Twofold Perkin condensation of 2,5-dibromophenylene-1,4-diacetic acid with arylglyoxylic acids followed by cyclo-dehydrobromination leads to dipyreno- and diperyleno-anthracene tetraesters and diimides. The imides show surprisingly large absorption shifts *versus* the esters, illustrating that electron-withdrawing substituents at the anthracene unit efficiently impart long wavelength absorption in such electrondeficient graphene nanoribbon fragments.

Oligocarboxylic derivatives of polycyclic arenes show great potential as particularly stable dyes and pigments for various applications including organic electronic devices. Vicinal pairs of carboxylic substituents - diester, imide, free diacid - can differ greatly in their solubilising and electronic effects, and thus present a means for the tuning of physical properties. This feature can be further reinforced if more than one vic-dicarboxylic moiety is incorporated into the molecule. For example, the electronic differences between tetraester and diimide derivatives of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) are manifest in the pronounced difference between their LUMO energies that make the diimides pronounced electron acceptors,¹ whereas the tetraesters can accept both holes and electrons, and thus can serve as an emitter layer in LEDs.^{2,3} The bathochromic effect of carboxylic substituents on the absorption of polycyclic arenes (perylene is yellow, its tetraesters are orange, its diimides are deep red) is of interest for the elaboration of longwavelength absorbing charge transport materials for organic photovoltaics. The reduction of the band gap of aromatic dyes towards values of inorganic semiconductors such as Si (1.1 eV) or GaAs (1.4 eV) is facilitated by carboxylic substituents because their bathochromic effect on sufficiently sextet-stabilised (and thus largebandgapped) arenes can help avoiding the use of highly reactive systems with weak sextet stabilisation such as pentacene.⁴ A current research target is the construction of large oligocarboxy-substituted

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small-bandgapped arenes by fusing two or more PTCDA moieties, directly or *via* the insertion of acene units. $^{5-7}$

A surprisingly overlooked and in our eyes particularly appealing strategy for the construction of *vic*-dicarboxy-substituted polycyclic arenes is what we have come to call the "glyoxylic" Perkin reaction, *i.e.* a variant of the Perkin reaction⁸ reported over 70 years ago by Koelsch and Wawzonek,⁹ where an arylglyoxylic acid is condensed with an arylacetic acid. To transform the resulting diarylmaleic acid into a fully condensed arene derivative, an *a priori* robust modern approach is the Pd-assisted elimination of HBr, recently optimised by Felpin and co-workers for similar mono-alkoxycarbonyl-substituted stilbene derivatives.¹⁰ This necessitates a bromine *ortho* to the acetic acid or the glyoxylic acid site in one of the Perkin reaction precursors.

Polycyclic arenes such as pyrene **1** and perylene **2** are often regiospecifically monosubstituted by Friedel–Crafts acylation adjacent to ring junctions,¹¹ leaving only one specific hydrogen-bearing *ortho* position open for post-Perkin ring closure. The reaction with ClCOCO₂Et is known to introduce a glyoxylic moiety into benzene, naphthalene, acenaphthene and thiophene,^{12–15} and we presumed it to be similarly feasible on larger arenes such as **1** and **2**. Selective *ortho*-bromination of the products on the other hand seemed not to be straightforward.

If no bromine can be easily introduced in a convenient position in the arylglyoxylic acid, then its introduction into the arylacetic acid must be considered. From the known 2-bromination of 4-cyanophenyl-acetic acid,¹⁶ we projected that *p*-phenylenediacetic acid **3** should easily undergo double bromination to yield a convenient substrate for twofold glyoxylic Perkin reactions followed by ring-closure. Thus, pairs of arylglyoxylic moieties would be fused *via* a tetrasubstituted anthracene moiety into large chromophores with modifiable functional substituents.

Indeed, we found that 2,5-dibromophenylene-1,4-diacetic acid 4 is obtained as the major bromination product, accompanied by 2,3-dibromophenylene-1,4-diacetic acid and smaller amounts of monobromo- and tribromo-phenylene-1,4-diacetic acid. The desired unpolar 2,5-isomer could be separated from the polar 2,3-isomer due to its lower solubility in the quite polar solvents THF and acetone and its higher solubility in the less polar solvent ethyl acetate, allowing its isolation on a 100 g scale in 44% yield.

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Having in hand a convenient dibrominated bifunctional building block for the assembly of large arenes by double glyoxylic Perkin reactions, we investigated the Friedel–Crafts acylation of **1** and **2** with ClCOCO₂Et. We found that in contrast to its reaction with acetyl, chloroacetyl or benzoyl chloride, **1** undergoes monoacylation predominantly with excess ClCOCO₂Et and AlCl₃ in DCM overnight, with only traces of diacylation products. A somewhat cleaner product is obtained if ZrCl₄ is used in place of AlCl₃, and ethyl pyrenyl-1-glyoxylate **5** is obtained on a 100 g scale in over 80% yield and saponified quantitatively to pyrenyl-1-glyoxylic acid **6** with aqueous sodium bicarbonate. The analogous reactions of perylene **2** produced ethyl perylenyl-3-glyoxylate **7** and its acid **8** in similar yields (Fig. 1).

Koelsch and Wawzonek's original procedure⁹ describes the reaction of potassium phenylglyoxylate with phenylacetic acid in



Fig. 1 Synthesis of dipyreno- and diperyleno-anthracenes *via* glyoxylic Perkin condensation and Pd-catalysed dehydrobromination. (a) NBS, $H_2SO_4-H_2O$, 25 °C, 16 h, 44%; (b) CICOCO₂Et, ZrCl₄, DCM, 25 °C, 16 h, 87%/79%; (c) NaHCO₃, EtOH-H₂O, reflux, 100%/95%; (d) NEt₃, Ac₂O, dioxane, reflux, 3 h, then addition of ROH, RBr, DBU, reflux, 16 h, 74%/73%; (e) Pd(OAc)₂, PCy₃, K₂CO₃, DMA, 110 °C, 20 h, 80%/81%; (f) (H(CH₂)₁₁)₂CHNH₂, imidazole, C₆H₄Cl₂, reflux, 16 h, 93%/89%. Oct = *n*-octyl, Undec = *n*-undecyl.

boiling Ac₂O for 12 h leading to diphenylmaleic anhydride, giving a yield of 43%.⁹ Fields *et al.*¹⁷ applied the same procedure to 3 and obtained phenylene-1,4-bis(phenylmaleic anhydride) in 88% yield within 1 h. This higher yield on a double reaction in much shorter time seems to indicate that unnecessarily long reaction times (or, by analogy, unnecessarily high reaction temperatures) may be detrimental. The Perkin reaction of benzaldehyde with sodium 1-bromo-2-naphthylacetate is reported to give a yield of only 34% under similar conditions¹⁸ (boiling acetic anhydride, 7 h), indicating that a sterically hindering *ortho*-bromo substituent might render the Perkin condensation less efficient.

To avoid the need to isolate a salt of the arylglyoxylic acid or the arylacetic acid, we conducted all Perkin condensation reactions with the free acids as starting materials and with triethylamine as base, as is standard in conventional (aldehydic) Perkin reactions.⁸ We found that cleaner products are obtained if the condensation is performed in refluxing dioxane or THF for a few hours, in the presence of a minor amount of acetic anhydride. As the purification of the poorly soluble bis(maleic anhydride)s is cumbersome, we esterified them directly *in situ* in the presence of excess DBU with 1-bromoalkane and the corresponding alkanol, a smooth procedure we have relied upon in the past.^{19–21} We thus obtained the fourfold esterified double condensation products of **4** with either **6** or **8** in satisfactory isolated overall yields of 74% and 73% in a one-pot procedure.

For both the pyrene and the perylene derived condensation products **9** and **10**, the ¹H-NMR spectra show very broad peaks for most of the aromatic protons and for the aliphatic protons of one of the two distinct pairs of alkyl chains, pointing to considerably sterically hindered rotation around the aryl–vinyl single C–C bonds. As these ¹H-NMR spectra did not allow a satisfactory identification of the Perkin condensation products, we were fortunate to obtain crystals suitable for X-ray crystallography from the pyrene-derived tetraethyl ester **9a**, confirming the presumed structure (see ESI[†]).

9 and 10 were smoothly doubly cyclised in 81% and 80% yield in DMA at 110 °C in the presence of Pd(OAc)₂, PCy₃ and K₂CO₃, following the procedures optimised for the cyclisation of 2-bromo-α-phenyl-trans-cinnamates.¹⁰ The resulting elongated fourfold alkoxycarbonyl-substituted dipyrenoanthracene 11 and diperylenoanthracene 12 (orange and red, respectively) again showed well-resolved ¹H-NMR spectra, evidencing their fully condensed structure with no slow internal rotations remaining. To transform the tetraesters 11 and 12 into their more electrondeficient diimide counterparts, we found that the isolation of the very insoluble dianhydrides or tetraacids can be avoided by directly reacting the tetraester with excess dialkylmethylamine and imidazole at 180 °C. If long amines are used that are not very miscible with imidazole, yields are improved using refluxing o-dichlorobenzene as the additional solvent besides excess imidazole.

Swallow-tailed amines R_2 CHNH₂ are known to induce far better solubilities in PTCDA-derived diimides and their higher rylene analogues^{22,23} than linear alkylamines. 6-Aminoundecane upon reaction with **11** yields a purple product which surprisingly proves to be insoluble in solvents such as chloroform or DCM. Longer 12-aminotricosane²⁴ yields a soluble diimide **12** in 93% yield. The striking colour change from orange to purple when transforming the tetraester **11** into diimide **13** corresponds to a 128 nm shift of



Fig. 2 Absorption spectra of dipyrenoanthracenes 11 & 13 (top) and diperylenoanthracenes 12 & 14 (bottom), 20 μ M in CHCl₃ (14: in 4: 1 CHCl₃ : Cl₂CHCHCl₂). Grey: tetraesters 11 and 12, black: diimides 13 and 14.

the main long-wavelength absorption peak from 447 nm to 575 nm (in CHCl₃, Fig. 2, top). This can be compared with the shift of 66 nm from PTCDA-derived orange tetraalkylesters (470 nm (ref. 25)) to their corresponding red bis(dialkylmethyl)imides (526 nm (ref. 26)). Similarly, tetraester **12** and 12-aminotricosane give diimide **14** in 89% yield, and here the colour change is even more striking, as red **12** transforms into deep green **14**, with a 132 nm shift of the longest-wavelength peak from 511 nm to 643 nm (Fig. 2, bottom), approaching the value of phthalocyanine (699 nm (ref. 27)).

With diperylenoanthracene, already the red tetraester **12** showed only a limited solubility even though we resorted to using relatively long octyl chains, compared to the dipyrenoanthracene analogue **11**, and the green diimide **14** is only very sparingly soluble in hot chloroform in spite of the presence of four undecyl side chains. It is more soluble in boiling *ortho*-dichlorobenzene or **1**,1,2,2-tetrachloroethane. The striking decrease in solubility from dipyrenoanthracenes **11** and **13**, with 42 carbon atoms in the polycyclic graphene segment, to diperylenoanthracenes **12** and **14**, with 50 carbons, parallels the dramatic decrease in solubility with increasing graphene segment size reported for the rylene-dialkylimide series.^{22,23}



Fig. 3 Swallow-tailed perylene-tetracarboxylic diimide (PTCDI) and naphthaleneor anthracene-fused PTCDI dimers **15** and **16**, with wavelengths of their longestwavelength absorption maxima in chloroform or DCM;^{6,7} **14**: 643 nm; R = n-alkyl.

Various approaches to chromophore extension *via* the fusion of perylene units onto acenes have been reported recently, including the lateral fusion of perylenediimides *via* an ethylene bridge to diperyleno-naphthalene-tetraimides **15**,⁶ or *via* a benzene bridge to diperyleno-anthracene-tetraimides **16**.⁷ In these cases, the bathochromic shift of the longest-wavelength absorption peak with respect to the corresponding PTCDIs is modest (19 nm for **15** and 36 nm for **16**, compared to 117 nm for **14**) (Fig. 3). Our approach is much more efficient in inducing longer wavelength absorption and thus a smaller band gap than the joining of electron-deficient perylene-diimides by non-electron-depleting acene units.

In summary, our methodology based on the glyoxylic Perkin reaction provides a short and straightforward synthetic access to dimers of polycyclic arenes fused by a central tetracarboxyanthracene moiety. The diimide derivatives absorb strongly bathochromically compared to the homologous tetraesters and to acene-fused PTCDI dimers, and thus represent a superior alternative to fusion of PTCDIs onto unsubstituted acenes as a means to impart smaller band gaps in electron deficient extended arene systems.

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Notes and references

- 1 E. Kozma and M. Catellani, Dyes Pigm., 2013, 98, 160.
- 2 T. Hassheider, S. A. Benning, H.-S. Kitzerow, M.-F. Achard and H. Bock, *Angew. Chem., Int. Ed.*, 2001, **40**, 2060.
- 3 I. Seguy, P. Jolinat, P. Destruel, R. Mamy, H. Allouchi, C. Courseille, M. Cotrait and H. Bock, *ChemPhysChem*, 2001, 2, 448.
- 4 E. Clar, *Polycyclic Hydrocarbons*, Academic Press and Springer-Verlag, London-New York, Berlin-Göttingen-Heidelberg, 1964.
- 5 H. Qian, F. Negri, C. Wang and Z. Wang, J. Am. Chem. Soc., 2008, 130, 17970.
- 6 Y. Li, C. Wang, C. Li, S. Di Motta, F. Negri and Z. Wang, Org. Lett., 2012, 14, 5278.
- 7 Z. Yuan, Y. Xiao and X. Qian, Chem. Commun., 2012, 46, 2772.
- 8 T. Rosen, Iridium Complexes Org. Synth., 1991, 2, 395.
- 9 C. F. Koelsch and S. Wawzonek, J. Org. Chem., 1941, 6, 684.
- 10 L. Nassar-Hardy, C. Deraedt, E. Fouquet and F.-X. Felpin, *Eur. J. Org. Chem.*, 2011, 4616.
- 11 Friedel-Crafts and related reactions, III: Acylation and related reactions, ed. G. A. Olah, Interscience Publishers, New York-London-Sydney, 1964.
- 12 G. Lock, Monatsh. Chem., 1955, 86, 511.
- 13 F. F. Blicke and R. F. Feldkamp, J. Am. Chem. Soc., 1944, 66, 1087.
- 14 G. Lock and R. Schneider, Chem. Ber., 1955, 88, 564.
- 15 R. G. Micetich, Org. Prep. Proced., 1970, 2, 249.
- 16 D. G. Cooper, I. T. Forbes, V. Garzya, D. J. Johnson, G. I. Stevenson and P. A. Wyman, *PCT Int. Appl. WO*, 2009037294, 2009.
- 17 E. K. Fields, S. J. Behrend, S. Meyerson, M. L. Winzenburg, B. R. Ortega and H. K. Hall Jr., *J. Org. Chem.*, 1990, 55, 5165.
- 18 C. L. Hewett, J. Chem. Soc., 1938, 1286.
- 19 J. Kelber, H. Bock, O. Thiebaut, E. Grelet and H. Langhals, *Eur. J.* Org. Chem., 2011, 707.
- 20 P. Sarkar, P. Dechambenoit, F. Durola and H. Bock, Asian J. Org. Chem., 2012, 1, 366.
- 21 J. Kelber, M.-F. Achard, B. Garreau-de Bonneval and H. Bock, *Chem.–Eur. J.*, 2011, **17**, 8145.
- 22 N. G. Pschirer, C. Kohl, F. Nolde, J. Qu and K. Müllen, Angew. Chem., Int. Ed., 2006, 45, 1401.
- 23 F. Nolde, W. Pisula, S. Müller, C. Kohl and K. Müllen, *Chem. Mater.*, 2006, **18**, 3715.
- 24 Z. Yuan, Y. Xiao, Y. Yang and T. Xiong, Macromolecules, 2011, 44, 1788.
- 25 M. J. Yang, S. L. Lu and Y. Li, J. Mater. Sci. Lett., 2003, 22, 813.
- 26 H. Langhals, Helv. Chim. Acta, 2005, 88, 1309.
- 27 J. H. Sharp and M. Lardon, J. Phys. Chem., 1968, 72, 3230.