

## Entry to Coronene Chemistry—Making Large Electron Donors and Acceptors

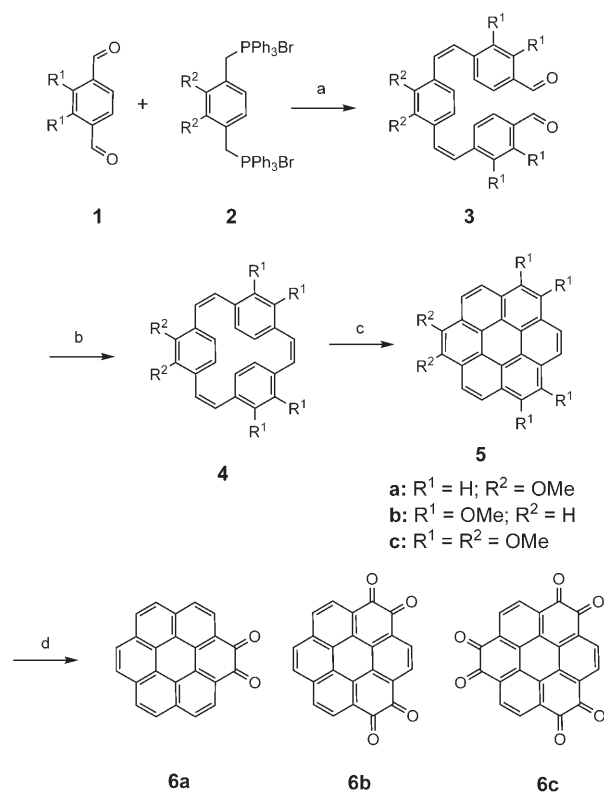
Ralph Rieger,<sup>[a]</sup> Marcel Kastler,<sup>[b]</sup> Volker Enkelmann,<sup>[a]</sup> and Klaus Müllen\*<sup>[a]</sup>

Single layers of graphite, commonly called graphenes, have recently attracted much attention.<sup>[1]</sup> It could be shown that graphenes are accessible by exfoliation from highly ordered pyrolytic graphite (HOPG), which led to a rapid development of this exciting research field.<sup>[2]</sup> These micrometer-sized layers show highly interesting properties, such as ballistic charge transport and the quantum Hall effect.<sup>[3,4]</sup> Nevertheless, the exfoliated graphenes are structurally not well defined. Small model systems of graphene have been synthesized with perfect structural control and hence defect-free.<sup>[5]</sup> One example of such nanographenes is hexa-*peri*-hexabenzocoronene (HBC), which serves as a semiconductor and even as a single-molecule transistor.<sup>[6,7]</sup> Much effort has been spent to increase the size of these nanographenes; however, the increase in size of these systems has always led to dramatic solubility problems.<sup>[8,9]</sup> Going to smaller but still relatively large nanographenes offers the possibilities of sublimation and crystallization. Hence, versatile ways of studying molecular properties on surfaces and crystals become available with highly developed techniques such as X-ray diffractometry and scanning tunneling microscopy.<sup>[10,11]</sup>

Coronene is in that sense a very promising  $D_{6h}$ -nanographene with a zigzag periphery and just the right size for processing techniques. Functionalized coronenes are, however, very rare.<sup>[12,13]</sup> To tune the electronic properties and intermolecular order, a versatile synthetic method is required to introduce substituents and control the symmetry of coronenes. This helps to match up the energetic levels of coronene with those of electrode materials, as needed for organic electronics. The symmetry plays a key role in crystal engi-

neering, for example, in the field of single-crystal semiconductors or charge transfer salts.<sup>[14,15]</sup>

Herein, we have synthesized a series of methoxy-substituted coronenes by converting paracyclophanes into coronenes by UV irradiation (Scheme 1).<sup>[16,17]</sup> In analogy to the method employed by Otsubo et al.,<sup>[18]</sup> a doubly *Z*-selective Wittig reaction was performed by reacting **1** and **2** at  $-40^{\circ}\text{C}$  in dichloromethane or dimethylformamide (DMF) by addition of lithium ethanolate. The dialdehyde **1** ( $\text{R}^1 = \text{OMe}$ ) is available by double lithiation of veratrol and subsequent



Scheme 1. Synthesis of three methoxy-substituted coronenes; conditions: a) LiOEt,  $-40^{\circ}\text{C}$ ,  $\text{CH}_2\text{Cl}_2$  or DMF, 27–46%; b)  $\text{TiCl}_4$ , Zn, THF, reflux, 34–48%; c) 300 nm 40 W, cyclohexane,  $\text{I}_2$ , 60–80%; d) 1.  $\text{BBBr}_3$ ,  $\text{CH}_2\text{Cl}_2$ , 2.  $\text{HNO}_3$ , 80–90%.

[a] R. Rieger, Dr. V. Enkelmann, Prof. Dr. K. Müllen  
Max-Planck-Institute for Polymer Research  
Ackermannweg 10, 55128 Mainz (Germany)  
Fax: (+49)6131-379-100  
E-mail: muellen@mpip-mainz.mpg.de

[b] Dr. M. Kastler  
BASF Aktiengesellschaft  
GKS/A - B1, 67056 Ludwigshafen (Germany)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200800832>.

treatment with DMF.<sup>[19]</sup> Compound **1** can be converted into compound **2** ( $R^2=OMe$ ) by reduction, followed by bromination, and reaction with triphenylphosphine. A high *Z*-selectivity of the Wittig reaction is needed to be able to close the molecule in a McMurry reaction to get to the [2.2.2]paracyclophanes **4** under pseudo-dilution conditions. A major side reaction is the formation of reduced aldehydes.

Irradiation of **4** in the presence of an oxidant such as iodine led to the corresponding coronenes **5** in high yield. In comparable stilbene systems the elimination of methoxy groups has been observed.<sup>[20]</sup> In the present case, only a few percent of side products that have lost methoxy groups are obtained. They can be separated easily by preparative chromatography. In contrast to the previous work of Otsubo et al.,<sup>[18]</sup> who only mention the formation of unsubstituted coronene as a side product in their experimental section, it is now possible to introduce functional groups and different symmetries, a fundamental requirement for further chemistry.

When the irradiation of **4c** is terminated after two hours, two intermediates are obtained, one of which could be identified as **4c'** by mass spectrometry and NMR analysis. The second compound is unstable and leads to the formation of coronene **5c** after a short time. It can be assumed to be **4c''**. This highly strained ring can thermally planarize and is oxidized by air. Therefore, it seems very likely that the reaction occurs stepwise as depicted in Figure 1.

In contrast to unsubstituted coronene and the analogous hexamethoxytriphenylene,<sup>[21]</sup> the methoxy-substituted coronenes are very soluble ( $>50 \text{ mg mL}^{-1}$  hexamethoxycoronene (**5c**) in dichloromethane, more than 10 times the solubility of hexamethoxytriphenylene). The methoxy groups are expected to increase the  $\pi$ - $\pi$  distance and therefore lead to a decrease in the intermolecular forces.

Treatment of **5a-c** with boron tribromide followed by oxidative workup gave the corresponding coronene quinones **6a-c**. The initially formed boron tribromide adducts of all of the coronenes are practically insoluble compounds that are hydrolyzed successfully only with concentrated nitric acid. All other attempted reactions ended with a black insoluble

material, possibly a pronounced network of partially hydrolyzed intermediates. In contrast to **6a** and **6b**, which are formed directly under these conditions, **6c** is only obtained after dissolution in dimethyl sulfoxide followed by treatment in air to quantitatively convert the hydroxy groups to ketones. Coronene-quinone (**6a**) has been reported previously by direct oxidation of coronene with chromium(VI) oxide.<sup>[22]</sup> Compounds **6b** and **6c** are reddish powders that are sparingly soluble in DMF and DMSO ( $1 \text{ mg mL}^{-1}$ ), but otherwise practically insoluble.

The reaction from **5c** to **6c** is remarkable as it converts the donor **5c** into a strong acceptor in just a single step—a very useful process with regard to the manifold of applications of donor-acceptor systems.<sup>[23,24]</sup> DFT calculations (Figure 2) reveal that the HOMO energy decreased by

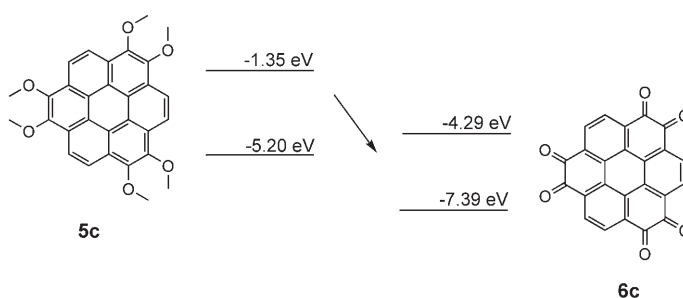


Figure 2. DFT calculations of the electronic states of **5c** and **6c** (B3LYP method, 6-31G\*\* basis set).

2.2 eV and that the LUMO value decreased by 2.9 eV. These values are supported by cyclic voltammetry data. Hexamethoxycoronene (**5c**) is oxidized at 0.74 V against ferrocene (standard), which corresponds to a value for the HOMO of  $-5.5 \text{ eV}$ .<sup>[25]</sup> Coronene-hexaone (**6c**) is reduced at  $-0.38 \text{ V}$  against ferrocene (standard), which corresponds to a value for the LUMO of  $-4.4 \text{ eV}$ . This is close to that for 7,7,8,8-tetracyanoquinodimethane (TCNQ), which is outstanding for discs of such a size.

Coronene-hexaone (**6c**) reacts with *o*-phenylenediamine as expected for  $\alpha$ -diketones by forming quinoxaline units

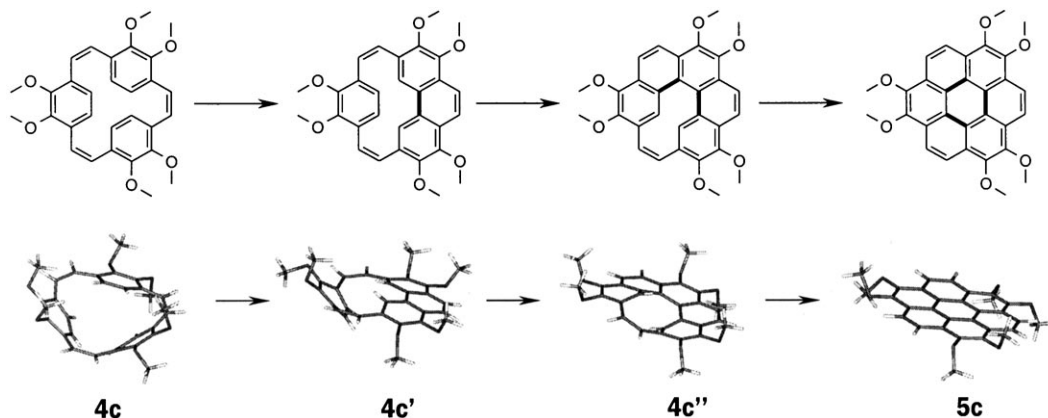
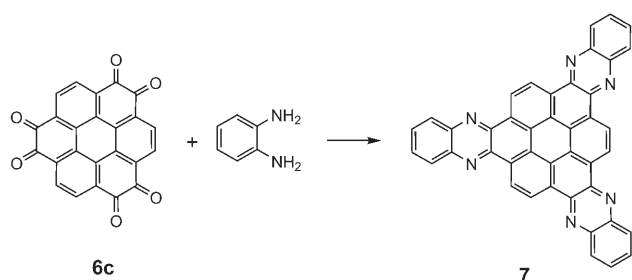


Figure 1. Planarization process of **4c** (calculated by Merck molecular force field (MMFF)).

(Scheme 2), which leads to the larger  $\pi$ -system **7**. Many more such extension reactions are conceivable, so **6c** offers a new platform for further chemistry and many more interesting molecules.



Scheme 2. Quinoxaline condensation of **6c**.

Figure 3 displays the electronic spectra of the methoxy-substituted coronenes. The main absorption peaks as well as the fluorescence peaks are almost identical with that of unsubstituted coronene. The methoxy groups thus influence the electronic structure only slightly, which is further supported by cyclovoltammetry (HOMO level at  $-5.5$  eV for all molecules). The lower symmetry of **5a** and **5b** in contrast to coronene ( $D_{3h}$  instead of  $C_{2v}$ ) leads to peak broadening particularly in the fluorescence spectra as more forbidden transitions become allowed when the symmetry is reduced.

A dramatic change in the absorption behavior can be observed when going from the methoxy-coronenes to the corresponding ketones **6a–c** (Figure 4). The main absorption is shifted to shorter wavelength, which is attributed to the fact that the  $\pi$  system of the disc has decreased. The interaction of the carbonyl bonds with the rest of the molecule creates more allowed transitions, a  $\pi$ - $n$  transition can be observed at a wavelength above 400 nm, which causes the reddish color of the substances. With an increasing number of carbonyl bonds, the bands become broader, which is another effect of the coupling between the aromatic core and the carbonyl groups.

Figure 5 depicts the single-crystal structures of **5a–c** together with that of unsubstituted coronene for comparison. Coronenes **5a** and **5b** form a herringbone-like, **5c** a sandwich-herringbone-like structure. The unsubstituted aromatic edge points towards the  $\pi$  system of the next disc, which is typical behavior for polyaromatic hydrocarbons

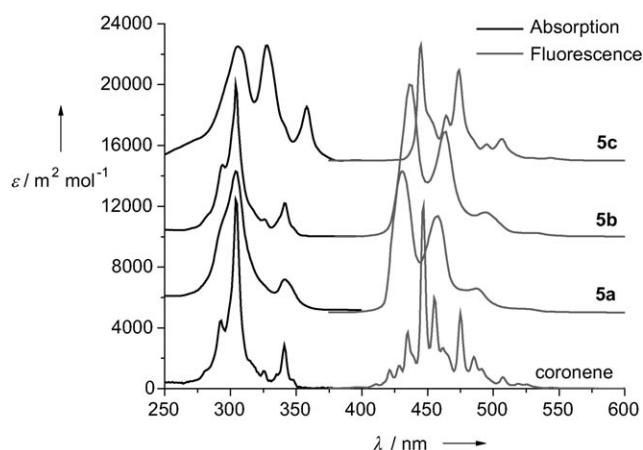


Figure 3. UV/Vis spectra of the methoxy-substituted coronenes **5a–c**; all recorded in cyclohexane ( $10^{-5}$  M), fluorescence excited at 280 nm.

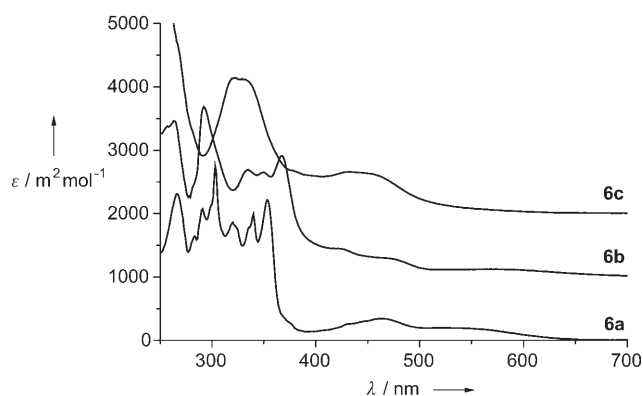


Figure 4. UV/Vis absorption spectra of the coronene ketones **6a–c**; all recorded in THF.

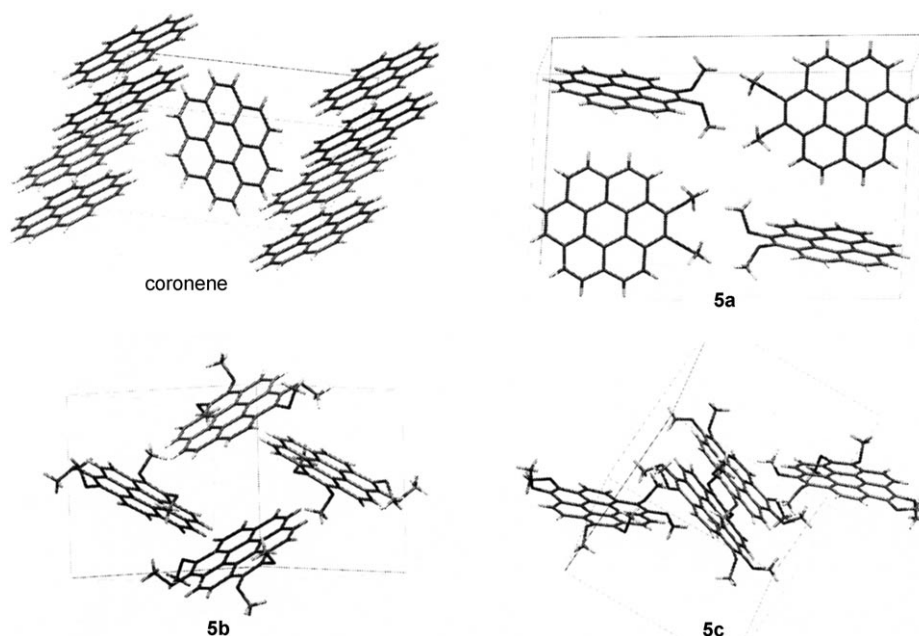


Figure 5. Single crystal structures of coronene and **5a–c**.<sup>[26]</sup>

(PAHs).<sup>[27]</sup> On the other hand, the methoxy groups maximize their mutual contact, presumably through dipolar interactions. Coronene **5a** even forms planes containing all the methoxy groups.

The interplane distance increases with the increasing number of methoxy groups. In the structure of **5a**, the discs are 3.4 Å apart, which is comparable to coronene, in **5b** the distance is 3.5 Å, and for **5c** it is 3.6 Å. This causes a decrease in the  $\pi$ - $\pi$  interaction and thus the observed increase in solubility as expected above.

Herein we have shown that the photochemical conversion of cyclophanes to coronenes is a very versatile method for the preparation of new coronene-based nanographenes with different functionality and symmetry. Coronenes with different degrees of methoxy substitution have been synthesized. Their absorption and emission as well as their packing in the crystal have been studied with regard to symmetry and number of substituents. These molecules can switch in just a single step from donors to strong acceptors by cleaving the ether group and oxidizing the alcohols to  $\alpha$ -diketones. Therefore, a set of new donor and acceptor molecules with a systematic variation of the electronic properties and the symmetry are available to investigate their properties as crystalline semiconductors, charge transfer systems, or metal-organic frameworks. Manifold known condensation reactions for  $\alpha$ -diketones can now be used to access a whole range of new molecules, one example has already been shown here. In the future, it should be possible to introduce further functionalities to coronene by making different cyclophanes. This will enable one to fully exploit the potential of coronene as a model system for graphene as well as to grow much larger systems, for example, by fusing appropriate precursors on surfaces.

### Acknowledgements

This work was financed by Deutsche Forschungsgemeinschaft (Korean German IRTG). R. R. thanks the "Fond der Chemischen Industrie" for financial support. We thank Dr. M. Wagner for NMR spectroscopy and many fruitful discussions.

**Keywords:** coronene • crystals • cyclophanes • donor-acceptor systems • photosynthesis

- [1] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183.
- [2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666.
- [3] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, S. Roth, *Nature* **2007**, *446*, 60.
- [4] J. R. Williams, L. DiCarlo, C. M. Marcus, *Science* **2007**, *317*, 638.
- [5] J. S. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718.
- [6] J. P. Hill, W. S. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii, T. Aida, *Science* **2004**, *304*, 1481.
- [7] A. Stabel, P. Herwig, K. Müllen, J. P. Rabe, *Angew. Chem.* **1995**, *107*, 1768–1770; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1609–1611.

- [8] M. Kastler, J. Schmidt, W. Pisula, D. Sebastiani, K. Müllen, *J. Am. Chem. Soc.* **2006**, *128*, 9526.
- [9] D. Wasserfallen, M. Kastler, W. Pisula, W. A. Hofer, Y. Fogel, Z. H. Wang, K. Müllen, *J. Am. Chem. Soc.* **2006**, *128*, 1334.
- [10] S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem.* **2007**, *119*, 4916; *Angew. Chem. Int. Ed.* **2007**, *46*, 4832.
- [11] M. E. Cañas-Ventura, W. Xiao, D. Wasserfallen, K. Müllen, H. Brune, J. V. Barth, R. Fasel, *Angew. Chem.* **2007**, *119*, 1846; *Angew. Chem. Int. Ed.* **2007**, *46*, 1814.
- [12] S. Alibert-Fouet, I. Seguy, J. F. Bobo, P. Destruel, H. Bock, *Chem. Eur. J.* **2007**, *13*, 1746.
- [13] H. C. Shen, J. M. Tang, H. K. Chang, C. W. Yang, R. S. Liu, *J. Org. Chem.* **2005**, *70*, 10113.
- [14] V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, J. A. Rogers, *Science* **2004**, *303*, 1644.
- [15] Y. Yamashita, M. Tomura, *J. Mater. Chem.* **1998**, *8*, 1933.
- [16] F. B. Mallory, C. W. Mallory, *Organic Reactions*, Vol. 30, Wiley, **1984**.
- [17] R. Gleiter, H. Hopf, *Modern Cyclophane Chemistry*, Wiley-VCH, **2004**.
- [18] T. Otsubo, R. Gray, V. Boekelheide, *J. Am. Chem. Soc.* **1978**, *100*, 2449. The cyclodehydrogenation of cyclophane to form coronene is only mentioned in the experimental part and does not appear in search engines like SciFinder or Crossfire Beilstein.
- [19] N. Kuhnert, G. M. Rossignolo, A. Lopez-Periago, *Org. Biomol. Chem.* **2003**, *1*, 1157.
- [20] F. B. Mallory, M. J. Rudolph, S. M. Oh, *J. Org. Chem.* **1989**, *54*, 4619.
- [21] S. Kumar, M. Manickam, *Chem. Commun.* **1997**, 1615.
- [22] A. Zinke, R. Ott, M. Sobotka, R. Kretz, *Monatsh. Chem.* **1952**, *83*, 546.
- [23] H. Meier, *Angew. Chem.* **2005**, *117*, 2536; *Angew. Chem. Int. Ed.* **2005**, *44*, 2482.
- [24] K. E. Sapsford, L. Berti, I. L. Medintz, *Angew. Chem.* **2006**, *118*, 4676; *Angew. Chem. Int. Ed.* **2006**, *45*, 4562.
- [25] A. J. Bard, L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, 2 ed., Wiley, **2001**.
- [26] Data collections for the crystal-structure analysis were performed on a Nonius KCCD diffractometer equipped with a Cryostream cooler with graphite-monochromated Mo<sub>K $\alpha$</sub>  radiation ( $\lambda = 0.7107$  Å). The samples were measured at 120 K. The structures were solved by direct methods (Shelxs) and refined on *F* with anisotropic temperature factors for the non-hydrogen atoms. The H atoms were refined with fixed isotropic temperature factors in the riding mode. **5a**: C<sub>26</sub>H<sub>16</sub>O<sub>2</sub>, *M<sub>r</sub>* = 360.41 gmol<sup>-1</sup>, monoclinic, space group *P2<sub>1</sub>/a*, *a* = 16.0660(6), *b* = 4.5830(4), *c* = 23.2180(7) Å,  $\beta = 99.842(1)^\circ$ , *V* = 1684.39(17) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}} = 1.421$  gcm<sup>-3</sup>,  $\mu = 0.089$ ,  $2\theta_{\text{max}} = 27.496^\circ$ , 22586 reflections measured, 3817 unique, 1854 observed, *R<sub>int</sub>* = 0.087, *R* = 0.0519, *R<sub>w</sub>* = 0.0432; **5b**: C<sub>28</sub>H<sub>20</sub>O<sub>4</sub>, *M<sub>r</sub>* = 420.46 gmol<sup>-1</sup>, monoclinic, space group *P2<sub>1</sub>/c*, *a* = 12.7901(6), *b* = 11.7359(5), *c* = 13.5211(6) Å,  $\beta = 107.344(1)^\circ$ , *V* = 1937.29(15) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}} = 1.442$  gcm<sup>-3</sup>,  $\mu = 0.096$ ,  $2\theta_{\text{max}} = 30.000^\circ$ , 21479 reflections measured, 5540 unique, 2224 observed, *R<sub>int</sub>* = 0.077, *R* = 0.0656, *R<sub>w</sub>* = 0.0299; **5c**: C<sub>30</sub>H<sub>24</sub>O<sub>6</sub>, *M<sub>r</sub>* = 480.52 gmol<sup>-1</sup>, monoclinic, space group *P2<sub>1</sub>/c*, *a* = 10.2336(5), *b* = 13.6684(5), *c* = 16.1664(6) Å,  $\beta = 101.541(1)^\circ$ , *V* = 2215.58(16) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}} = 1.440$  gcm<sup>-3</sup>,  $\mu = 0.100$ ,  $2\theta_{\text{max}} = 29.499^\circ$ , 28868 reflections measured, 6095 unique, 1726 observed, *R<sub>int</sub>* = 0.076, *R* = 0.0491, *R<sub>w</sub>* = 0.0536; CCDC-678259, CCDC-678260, and CCDC-678261 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- [27] G. R. Desiraju, A. Gavezzotti, *Acta Crystallogr. B* **1989**, *45*, 473.

Received: May 2, 2008  
Published online: June 3, 2008