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From π-expanded coumarins to π-expanded pentacenes

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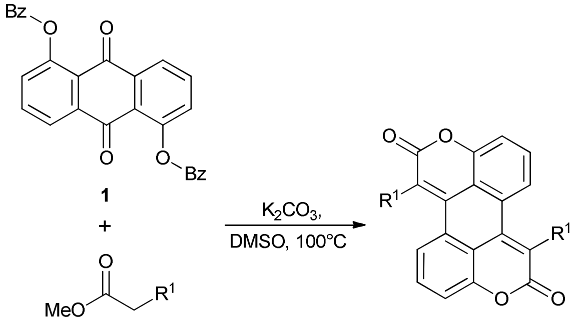
The synthesis of two novel types of π-expanded coumarins has been developed. Modified Knoevenagel bis-condensation afforded 3,9-dioxa-perylene-2,8-diones. Subsequent oxidative aromatic coupling or light driven electrocyclization reaction led to dibenzo-1,7-dioxacoronene-2,8-dione. Unparalleled synthetic simplicity, straightforward purification and superb optical properties have a potential to bring these perylene and coronene analogs towards various applications.

π-Expanded coumarins have attracted considerable attention in recent years. The growing number of their possible applications, including two-photon fluorescence microscopy,[1] OLEDs,[2] dye-sensitized solar cells,[3] energy and electron transfer systems[4] and fluorescent probes,[5] significantly accelerates the progress in the synthesis of coumarins. Noticeably, the extension of coumarin π-systems can be achieved through multiple methods. Recent activity in this area proved that fused rings introduced as structural elements constitute a powerful approach to control photophysical properties of these chromophores, therefore, a large number of simple benzocoumarins have been studied over years,[6] including heteroatom analogues.[7] Among coumarins π-expanded at positions 4 and 5, many 4-oxa-5-oxopyrene analogs have also been synthesized,[8] and isolated from orchids.[9] Recently the first total synthesis has been reported for santiagonamine isolated from stems and branches of South American shrub *Berberis darwinii*.[10] Moreover, many benzocoumarins exhibit strong biological activity.[11] Encouraged by great applicability of these aromatic compounds, we decided to examine the synthesis and photophysical properties of previously unknown family of π-expanded coumarins – namely new hybrids constructed from two coumarin units linked in head-to-tail manner.

Klimenko and co-workers discovered that reaction of 1-acetoxyantraquinone with phenylacetonitrile led to the mixture of a π-expanded furan derivative and compound bearing coumarin unit.[12] In our approach, we reasoned that starting from the corresponding 1,5-dibenzoyloxyantraquinone (**1**) an analogous reaction would lead to coumarin **7** (Scheme 1). Unfortunately, complex mixture of highly coloured products was formed under the original reaction conditions. Thus, we decided to use phenylacetic acid methyl ester (**2**) instead of nitrile, which led to the formation of strongly fluorescent yellow compound, which after simple work-up and NMR and MS analysis was confirmed to be desired bis-coumarin **7** (73% yield, Scheme 1). The same procedure could easily be applied to phenylacetic acid esters bearing both electron-donating and electron-accepting groups, as well as to the heterocyclic analogs **3**-**6**, leading to bis-coumarins **8**-**11** in yields 48-83% (Scheme 1). Five different perylene analogues have been synthesized, which were subsequently subjected to oxidative aromatic coupling. It is important to emphasize that all attempts to perform this condensation from esters of aliphatic acids failed. Reactions of compound **1** with such substrates as methyl propionate, ethyl acetoacetate and diethyl malonate failed to lead to any identifiable products. We believed that the fusion of additional two benzene ring, resulting in further elongation of the π-system, would have substantial effect on the photophysical properties.

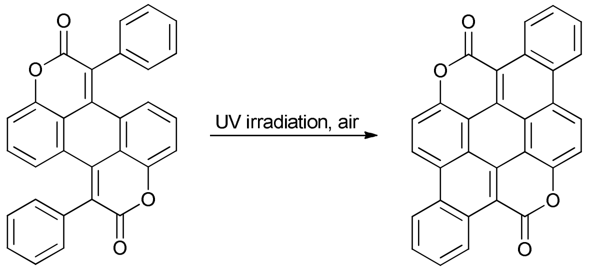


2. R = Ph	**7**. R = Ph	73%
3. R = 4-MeOC$_6$H$_4$O	**8**. R = 4-MeOC$_6$H$_4$	54%
4. R = 3,4-(MeO)$_2$C$_6$H$_3$	**9**. R = 3,4-(MeO)$_2$C$_6$H$_3$	83%
5. R = 2-Thienyl	**10**. R = 2-Thienyl	48%
6. R = 4-FC$_6$H$_4$	**11.** R = 4-FC$_6$H$_4$	53%

Scheme 1.

Interestingly, we found that compound **7** is unstable in solution under sunlight or UV irradiation at 365 nm. Both natural (sunlight) and artificial irradiation led to exactly the same product **12**, but with slightly lower yield in the case of UV irradiation (Scheme 2). Dye **12** however, proved to be very weakly soluble in organic solvents. Such light-driven dehydrogenations are generally known and have been previously used for the stilbene-phenanthrene phototransformation,[8f,13] however, the only example of coumarins resembling oxacoronenone structure was described by Zinke in

1953.[14] The same conditions applied to oxidation of compounds **8** and **9** led again to dramatic decrease in solubility of the product. The NMR spectra were difficult to interpret unambiguously and the mass spectra were the only evidence for the existence of new coronene analogues. Thus, we decided to replace methoxy substituents in **9** with hexyloxy groups, which should break π-π interaction due to higher steric hindrance. After treatment of **9** with BBr_3, 4-fold demethylation took place and the resulting phenol was immediately transformed into hexyl ether **13** under standard Williamson conditions in good yield (Scheme 3). The obtained product was used for photocyclization. After irradiation in the presence of air (UV-lamp, 365 nm) we obtained compound **14** in 54% yield. As expected, compound **14** had moderate solubility in selected solvents, which allowed for a full characterization using ^{1}H NMR ^{13}C NMR, COSY, HSQC, HMBC and MS. Subsequently, we performed the transformation of **13** into **14** under oxidative aromatic coupling, ($FeCl_3$, $BF_3{\cdot}OEt_2$, CH_2Cl_2),[15] which resulted in higher yield (87%). Both reactions are regioselective and lead to the product with lower steric hindrance.

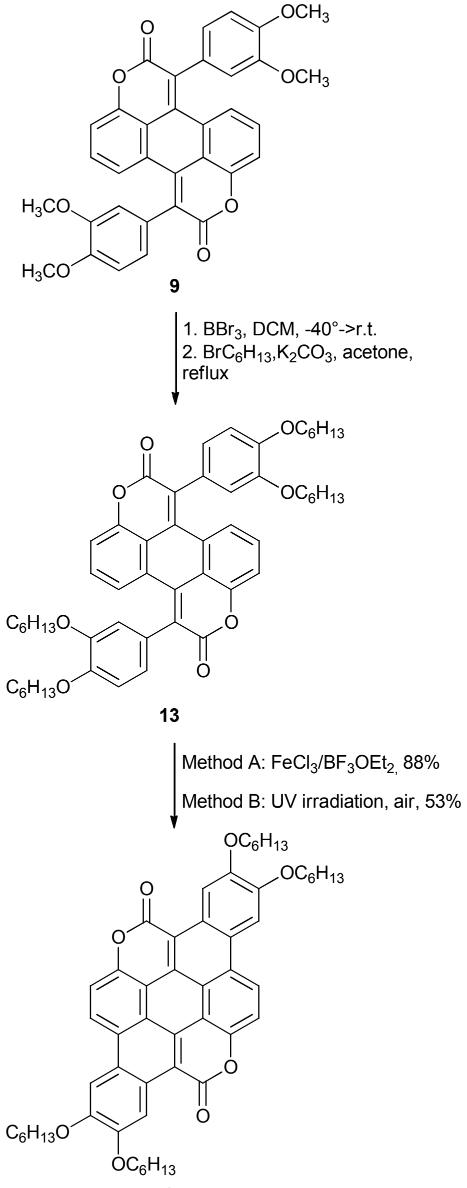


7 **12**

Scheme 2

The spectral characteristics were examined for compounds **7-11**, **14** and were subsequently compared to those of perylene, pentacene and 7-hydroxycoumarin (Table 1, Fig. 1). The analysis carried out for the absorption spectra taken for compounds **7-11** showed that the introduction of electron-donating substituents into a new 3,9-dioxaperylene-2,8-dione system, influences both the absorption and emission properties of these heterocycles (bathochromic shift ~50 nm). Very strong red-shift of absorption (dye **14** - 142 nm) and emission, observed upon addition of four alkoxyl groups to planar dye **12**, is due to the stronger influence of oxygen lone electron pairs with planar chromophore. The electronic spectra of new heterocycles differ in the shape. Due to a more rigid structure, compounds **12** and **14** is characterized by a well resolved structure, while dyes **7-11** show unstructured absorption bands. Fluorescence quantum yields determined for dyes **7-11** are moderate (Φ_{fl} = 10-30%) and the Stokes shifts are rather large (5000-7000 cm^{-1}).

It is reasonable therefore, to assume that aryl substituents in dyes **7-11** do not overlap with π-system of the main chromophore in the ground state (due to steric hindrance with hydrogens at bay position) but their geometry alters in the excited state. The drastic change in fluorescence quantum yield between dyes **7-11** and fully fused compound **14** (Φ_{fl} = 90%) can be associated to the effect of more flexible molecular structure of series **7-11** (Table 1, Fig. 1). When compared with well-known coumarin derivatives such as 7-hydroxycoumarin (7-HC), benzo[*f*]coumarin (B[*f*]C) and benzo[*g*]coumarin (B[*g*]C), compounds **7-11** possess bathochromically shifted absorption and emission as well as higher fluorescence quantum yield (Table 1). Typically, coumarins lacking electron-donating group at position 7 possess negligible Φ_{fl}.[16] In contrast, for 3,9-dioxaperylene-2,8-diones **7-11** fluorescence quantum yield is virtually independent on substituent orientation in benzene ring (Table 1).



Scheme 3

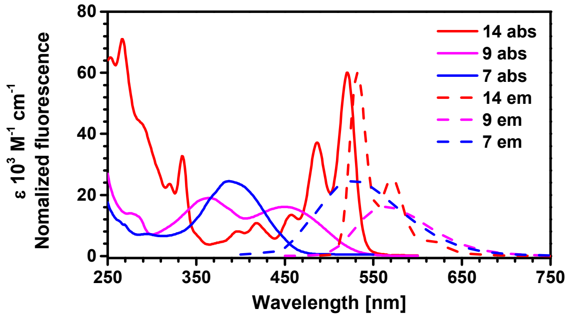


Figure 1. Absorption (solid) and emission (dashed) spectra of compounds **7**, **9** and **14** in $CHCl_3$ at room temperature.

When compared with perylene compounds **7-11** have much stronger absorption but not bathochromically shifted absorption and appreciably bathochromically shifted emission. In contrast dibenzo-1,7-dioxacoronene-2,8-dione **14** being formally π-expanded pentacene has different optical properties. The fluorescence quantum yield is almost quantitative but absorption is strongly hypsochromically shifted (Table 1). Dye **14** comprises a unit of 5,6:12,13-dibenzopentacene, very rarely studied hydrocarbon,[17] which also has hypsochromically shifted absorbance versus pentacene (λ_{abs} = 400, 430 nm). The optical properties of dye **14** bear also some resemblance to 1,14:11,12-dibenzopentacene,[18a] 1,14:7,8-dibenzopentacene,[18a] 1,2:1,14-dibenzopentacene,[18b] 7,8:1,12-dibenzopentacene,[18c] and tetraphenyldibenzoperiflanthene[18d] but molar absorption coefficients of the latter ones are higher. Still, the advantage of compounds **12** and **14** are much more straightforward synthesis and typically stronger emission.

Table 1. Photophysical properties (in $CHCl_3$) determined for synthesized compounds and their analogs[a]

compd	λ_{abs}, nm ($\varepsilon\cdot\times10^{-3}$)	λ_{em}, nm (Φ_{fl})[b,c]	τ (ns)[b]	k_f (10^8 s^{-1})[d]	k_{nr} (10^8 s^{-1})
7	385 (24.5)	527 (0.16)	1.1	1.5	7.6
8	433 (18.5)	613 (0.25)	2.4	1.1	3.1
9	450 (16.0)	565 (0.10)	1.6	0.6	5.6
10	445 (15.0)	535, 610 (0.31)	0.8	3.9	8.6
11	385 (30.0)	535 (0.15)	2.7	0.6	3.2
12[e]	378	460, 472	-	-	-
14	520 (60.0)	571, 615 (0.90)[e]	4.8	1.9	0.2
7-HC[f]	325 (4.11)[e]	410 (0.07)[e]	-	-	-
B[*f*]C[f]	275 (10.2)	425 (0.08)	-	-	-
B[*g*]C[f]	321 (19.0)	429 (0.11)	-	-	-
perylene[f]	439 (4.55)	446, 504 (0.94)	-	-	-
pentacene[f]	580	595 (0.08)	-	-	-

[a] concentrations of compounds were in the range of 5-7 μM; [b] λ_{ex}=320 nm, ± 0.1; [c] measured using integrating sphere; [d] ± 0.1; [e]due to extremely low solubility of **12** only qualitative absorption and emission spectra were recorded; [f]ref. 16

Conclusions

In summary, we report the discovery of two unprecedented π-expanded heterocyclic scaffolds bearing two coumarin cores. The proposed synthetic method is operationally simple and leads to analogs of perylene and pentacene in 2-3 steps. The examination of spectroscopic properties of all new compounds, which are formally π-expanded coumarins, showed that they displayed intense fluorescence. The smooth photochemical transformation of 3,9-dioxa-perylene-2,8-diones into dibenzopentacenes under open-air-conditions opens new possibilities towards the synthesis of large π-expanded heterocyclic analogs of PAHs. The use of presented approach can lead to a wide range of previously unknown heterocycles, which can serve as ideal platforms in such diverse areas as molecular electronics and fluorescent imaging.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details for compounds **7-11** and **14**, ^1H NMR, ^{13}C NMR spectra, powder XRD, fluorescence decays. For ESI see DOI: 10.1039/c000000x/

1 (a) I. Kim, D. Kim, S. Sambasivan and K. H Ahn, *Asian J. Org. Chem.*, 2012, **1**, 60-64. (b) D. Kim, S. Singha, T. Wang, E. Seo, J. H. Lee, S.-J. Lee, K. H. Kim and K. H. Ahn, *Chem. Commun.*, 2012, **48**, 10243-10245.

2 (a) Z. Liu, M. G. Helander, Z. Wang and Z. Lu, *J. Phys. Chem. C*, 2010, **114**, 11931-11935. (b) H. Zhang, T. Yu, Y. Zhao, D. Fan, D. Xia and P. Zhang, *Synth. Met.*, 2010, **160**, 1642-1647.

3 A. Mishra, M. K. R. Fischer and P. Bäuerle, *Angew. Chem. Int. Ed.*, 2009, **48**, 2474-2499.

4 (a) M. Tasior, D. T. Gryko, D. Pielacińska, A. Zanelli and L. Flamigni, *Chem. Asian J.*, 2010, **5**, 130-140. (b) M. Tasior, R. Voloshchuk, Y. M. Poronik, T. Rowicki and D. T. Gryko, *J. Porphyrins Phthalocyanines*, 2011, **15**, 1011-1023.

5 (a) K. Tsukamoto, Y. Shinohara, S. Iwasaki and H. Maeda, *Chem. Commun.*, 2011, **47**, 5073-5075. (b) K. G.; Reddie, W. H. Humphries, C. P. Bain, C. K. Payne, M. L. Kemp and N. Murthy, *Org. Lett.*, 2012, **14**, 680-683.

6 (a) E. J. Carlson, A. M. S. Riel and B. J. Dahl, *Tetrahedron Lett.*, 2012, **53**, 6245-6249. (b) J. Luo, Y. Lu, S. Liu, J. Liu and G.-J. Deng, *Adv. Synth. Catal.*, 2011, **353**, 2604-2608. (c) Y. Li, Y.-J. Ding, J.-Y. Wang and X.-S. Su Wang, *Org. Lett.*, 2013, **15**, 2574-2577. (d) T. N. Poudel and Y. R. Lee, *Org. Biomol. Chem.*, 2014, **12**, 919-930. (e) K. Inamoto, J. Kadokawa and Y. Kondo, *Org. Lett.*, 2013, **15**, 3962-3965. (f) O. S. Wolfbeis, *Monatsh. Chem.*, 1978, **109**, 1413-1421.

7 (a) J. Chen, W. Liu, J. Ma, H. Xu, J. Wu, X. Tang, Z. Fan and P. Wang, *J. Org. Chem.*, 2012, **77**, 3475-3482.

8 (a) R. G. Gillis and Q. N. Porter, *Aust. J. Chem.*, 1989, **42**, 1007-1010. (b) R. Ott and A. Zinke, *Monatsh. Chem.*, 1953, **84**, 1132-1139. (c) A. Zinke and W. Zimmer, *Monatsh. Chem.*, 1951, **82**, 348-358. (d) T. Kimura, M. Minabe and K. Suzuki, *J. Org. Chem.*, 1978, **43**, 1247-1248. (e) S. A. Glover, S. L. Golding, A. Goosen and A. McCleland, *J. Chem. Soc. Perkin 1*, 1981, 842-848. (f) W. Dilthey and H. Giebert, *Chem. Ber.*, 1942, **75**, 211-215. (g) Y. Tominaga, L. W. Castle and R. N. Castle, *J. Heterocyclic Chem.*, 1996, **33**, 1017-1018.

9 (a) M. U. Bhaskar, L. J. M. Rao, N. S. P. Rao and P. R. M. Rao, *Phytochemistry*, 1989, **28**, 3545-3546. (b) A. Arnone, G. Nasini and O. V. de Pava, *Phytochemistry*, 1991, **30**, 2729-2731.

10 M. D. Markey, Y. Fu and T. R. Kelly, *Org. Lett.*, 2007, **9**, 3255-3257.

11 (a) G. Cozza, A. Gianoncelli, P. Bonvini, E. Zorzi, R. Pasquale, A. Rosolen, L. A. Pinna, F. Meggio, G. Zagotto and S. Moro, *ChemMedChem.*, 2011, **6**, 2273-2286. (b) L. G. Hamann, R. I. Higuchi, L. Zhi, J. P. Edwards, X. N. Wang, K. B. Marschke, J. W. Kong, L. J. Farmer and T. K. Jones, *J. Med. Chem.*, 1998, **41**, 623-639. (c) L. Pisani, M. Catto, I. Giangreco, F. Leonetti, O. Nicolotti, A. Stefanachi, S. Cellamare and A. Carotti, *ChemMedChem.*, 2010, **5**, 1616-1630. (d) J. Novak and C. A. Salemink, *J. Chem. Soc. Perkin Trans.*, 1983, 2867-2871.

12 L. Ya. Mainagashev and L. S. Klimenko, *Russian Chem. Bull.*, 1996, **45,** 2569-2573.

13 (a) S. Pogodin and I. Agranat, *J. Am. Chem. Soc.*, 2003, **125**, 12829–12835 (b) F. D. Lewis, R. S. Kalgutkar and J.-S. Yang, *J. Am. Chem. Soc.*, 2001, **123**, 3878. (c) H. Yu, J. Li and Z. Kou, *J. Org. Chem.*, 2010, **75**, 2989-3001. (d) J. N. Moorthy, S. Mandal, A. Mukhopadhyay and S. Samanta, *J. Am. Chem. Soc.*, 2013, **135**, 6872–6884.

14 O. Zinke, *Monatshefte fuer Chemie*, 1953, **84**, 1131-1139.

15 (a) M. Grzybowski, K. Skonieczny, H. Butenschön and D. T. Gryko, *Angew. Chem. Int. Ed.*, 2013, **52**, 9900-9930. (b) E. Faggi, R. Sebastián R. Pleixats, A. Vallribera, A. Shafir, A. Rodríguez-Gimeno and R. Ramírez de Arellano, *J. Am. Chem. Soc.*, 2010, **132**, 17980–17982.

16 (a) S. L. Murov, I. Carmichael, G. L. Hug, Handbook of Photochemistry, Marcel Dekker, 1993, New York. (b) C. Murata, T. Masuda, Y. Kamochi, K. Todoroki, H. Yoshida, H. Nohta, M. Yamaguchi, A. Takadate, *Chem. Pharm. Bull.*, 2005, **53**, 750-758.

17 E. A Braude, J. S. Fawcett and A. A. Webb, *J. Chem. Soc.*, 1954, 1049.

18 (a) Y. Li, K.-W. Huang, Z. Sun, R. D. Webster, Z. Zeng, W. Zeng, C. Chi, K. Furukawa and J Wu, *Chem. Sci.*, 2014, **5**, 1908. (b) B. Boggiano and E. Clar, *J. Chem. Soc.*, 1957, 2681. (c) J. Xiao, Y. Divayana, Q. Zhang, H. M. Dong, H. Zhang, F. Boey, X. W. Sun and F. Wudl, *J. Mat. Chem.*, 2010, **20**, 8167. (d) J. D. Debad, J. C. Morris, V. Lynch, P. Magnus and A. J. Bard, *J. Am. Chem. Soc.*, 1996, **118**, 2374-2379.

Table of contents graphic and text:

Dihydroxyantraquinone can be transformed into head-to-tail bis-coumarin which undergo photo-dehydrogenative coupling leading to coronene derivatives.