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Anthradifuran, a Furan Analogue of Pentacene, and Its Isomers, Exhibiting Solid-state Photoluminescence

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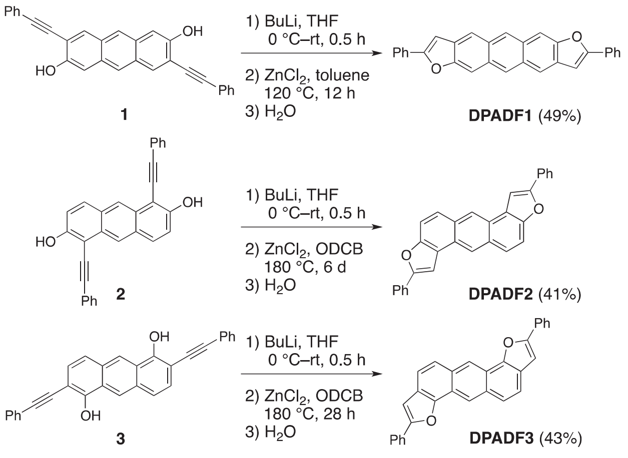
We have synthesized diphenyl-substituted anthra[2,3-*b*:6,7-*b*′]difuran, a furan analogue of pentacene, together with its isomers, anthra[2,1-*b*:6,5-*b*′]difuran and anthra[1,2-*b*:5,6-*b*′]difuran. These compounds are stable in the solid state with high decomposition temperatures. They are luminescent in the solid state with a quantum yield of 0.093–0.23.

Acenes[1] play an important role in organic functional materials.[2] A representative compound, pentacene,[3] is unstable in air, and to remedy this problem, heteroacenes,[4] such as thienoacenes, have been synthesized, and their superior stability and properties in several respects have been reported.[5] We recently demonstrated the utility of fused furans, which have received much less attention as functional materials than have thiophenes. Thus, we have reported the unique photophysical properties of benzodifurans (BDFs) as well as their high carrier mobilities in the amorphous state, making them suitable for applications as hole-transporting materials and as host materials in organic light-emitting diodes (OLEDs).[6] We have also found that single crystals of naphthodifurans (NDFs) serve as active materials in organic field-effect transistors (OFETs) with high hole mobilities.[7] Here, we report the synthesis, structure, and photophysical properties of linearly fused anthra[2,3-*b*:6,7-*b*′]difuran (**ADF1**), in which the anthradifuran (ADF) core has a structure that is isoelectronic with pentacene. We also synthesized its zigzag-shaped isomers, anthra[2,1-*b*:6,5-*b*′]difuran (**ADF2**) and anthra[1,2-*b*:5,6-*b*′]difuran (**ADF3**), having a structure that is isoelectronic with dibenzo[*a*,*h*]anthracene. Their stability and photoluminescent properties in the solid state are also described.[8]

ADF compounds were synthesized using the recently developed zinc-mediated double cyclization reaction (Scheme 1).[6a,9] Thus, 3,7-dialkynylanthracene-2,6-diol **1** was lithiated with butyllithium, transmetallated to zinc, and heated at 120 °C. An internal addition of the zinc phenolate to the alkyne moiety furnished **DPADF1** as an orange solid. Because the solubility of **DPADF1** in organic solvents is very low, the crude product was sublimed to obtain a pure product in 49% yield. The product was characterized by NMR, mass spectrometry, and X-ray analysis, and its purity was confirmed by elemental analysis (see details in Supporting Information; SI[19]). The cyclization reactions of **2** and **3** required a slightly higher reaction temperature (180 °C) and afforded **DPADF2** and **DPADF3** as yellow solids in 41% and 43% yields after sublimation. The compounds sublime at >380 °C without decomposition (see SI[19]). Thin films of these three compounds after exposure for a long time to air showed no change in their UV–vis spectra, indicating air stability in the solid state, while **DPADF1** was gradually oxidized in solution under ambient conditions.



Scheme 1.

Single-crystal X-ray analysis showed that the **ADF** core is very flat and the phenyl substituents are almost coplanar with the **ADF** core, as shown in Figure 1 (details are given in SI).[10,19] The crystal packing of **DPADF1** was in a herringbone arrangement (Figure 1a), similar to that of the polymorphic crystal structures of pentacene,[11] with short intermolecular contacts of 2.79 Å for C···H. In contrast, **DPADF2** molecules are stacked along the *b* axis with an interplanar distance of 3.53 Å (Figure 1b). Similarly, **DPADF3** molecules stack along the *a* axis with interplanar distances of 3.44–3.46 Å (Figure 1c). The different packing of **DPADF1** from the other compounds is due to the CH/π interaction resulting from the linear molecular shape of **DPADF1**.

Photophysical property measurements of **ADF**s in the solid state revealed a difference in absorption between the linear- and the zigzag-fused **ADF**s, as well as in their emission properties (Figure 2 and Table 1). Absorption bands showed a well-defined vibronic fine structure because of the rigidity of the **ADF** framework. Not surprisingly, the linear **DPADF1** showed a much longer absorption maximum (540 nm) than the zigzag molecules did (451 and 417 nm for **DPADF2** and **DPADF3**, respectively), as reported for pentacene and dibenzo[*a*,*h*]anthracene.[12] The **ADF**s showed photoluminescence in the solid state. The emission bands are close to being mirror images of the absorption spectra. **DPADF1** showed an orange emission with a maximum wavelength of 593 nm, while **DPADF2** and **DPADF3** showed a yellow-green emission at 515 and 489 nm, respectively. The photoluminescence quantum yields (Φ_{PL}) were 0.093, 0.23, and 0.15 for **DPADF1**, **DPADF2**, and **DPADF3**, respectively. The fact that the **ADF**s emit in the solid state stands in sharp contrast to pentacene and the thiophene counterparts,

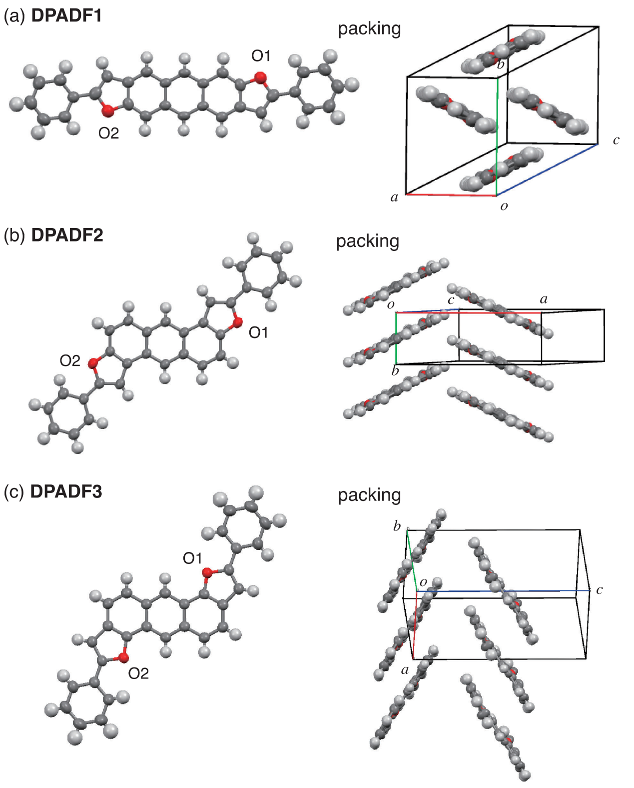


Figure 1. X-ray crystallographic structures of the **DPADF** compounds. Left column: ORTEP drawing (50% probability for thermal ellipsoids). Right column: packing structures with unit lattice (viewed from an arbitrary direction).

Table 1. Summary of the properties of the **ADF** compounds

Compound	λ_{abs} [nm][a]	λ_{em} [nm] (Φ_{PL})[b]	IP [eV][c]
DPADF1	540	593 (0.093)	5.1
DPADF2	451	515 (0.23)	5.5
DPADF3	417	489 (0.15)	5.2

[a] UV–vis absorption maximum wavelength in a thin film. [b] Emission maximum wavelength in the solid state. Emission quantum yields are shown in parentheses. [c] Ionization potential determined from photoemission yield spectroscopy measurements.

which show no or little photoluminescence in the solid state.[13] The ionization potentials (IPs) of films determined by photoemission yield spectroscopy (PYS; Table 1 and SI)[14,19] were 5.1, 5.5, and 5.2 eV for **DPADF1**, **DPADF2**, and **DPADF3**, respectively. These IPs are larger than the value for pentacene (4.9 eV) and comparable with a thiophene analogue (5.1 eV),[15] which are known to serve as good semiconducting materials.

In summary, being chemically and thermally stable, the linear- and the zigzag-fused **ADF**s add to the rapidly expanding repertoire of furan compounds for organic electronic applications.[16–18] Their photoluminescence ability in the solid state illustrates the difference from the popular thiophene analogues, which deserves further studies in the area of both chemistry and materials science, and their application is currently under investigation.

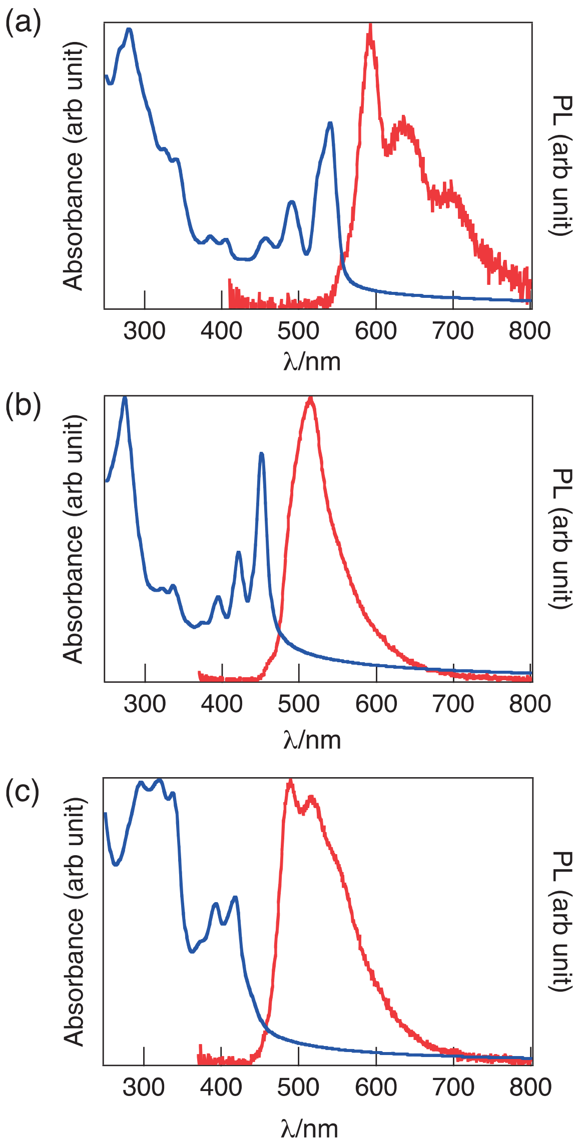


Figure 2. Photophysical properties of **ADF**s in the solid state (blue: absorption spectra of thin film, red: photoluminescence spectra of powder). (a) **DPADF1**, (b) **DPADF2**, and (c) **DPADF3**.

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10 Single crystals suitable for X-ray analysis were obtained by physical vapor transport (PVT) for **DPADF1** and **DPADF3**, and recrystallization from hot chloroform for **DPADF2**. Crystal data for **DPADF1**: $C_{30}H_{18}O_2$, $M_r = 410.44$, $T = 296\,K$, triclinic, space group $P\bar{1}$, $a = 5.8523(6)\,Å$, $b = 7.8526(9)\,Å$, $c = 21.788(3)\,Å$, $\alpha = 98.201(7)°$, $\beta = 97.343(7)°$, $\gamma = 92.859(6)°$, $V = 980.53(19)\,Å^3$, $Z = 2$, $R1 = 0.0744$ (1436 with $I > 2\sigma(I)$), $wR = 0.2486$ (all data), GOF = 0.987. **DPADF2**: $C_{30}H_{18}O_2$, $M_r = 410.44$, $T = 296\,K$, monoclinic, space group $P2_1/n$, $a = 12.0004(2)\,Å$, $b = 3.92490(10)\,Å$, $c = 21.0042(4)\,Å$, $\beta = 99.8721(13)°$, $V = 974.66(4)\,Å^3$, $Z = 2$, $R1 = 0.0583$ (965 with $I > 2\sigma(I)$), $wR = 0.2079$ (all data), GOF = 1.064. **DPADF3**: $C_{30}H_{18}O_2$, $M_r = 410.44$, $T = 296\,K$, triclinic, space group $P\bar{1}$, $a = 6.5300(2)\,Å$, $b = 10.7220(3)\,Å$, $c = 14.9626(5)\,Å$, $\alpha = 78.7993(18)°$, $\beta = 84.1453(18)°$, $\gamma = 87.279(2)°$, $V = 1021.88(5)\,Å^3$, $Z = 2$, $R1 = 0.0412$ (2924 with $I > 2\sigma(I)$), $wR = 0.1161$ (all data), GOF = 1.060.

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