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Synthesis and Characterization of Two Different Azarubrenes

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The synthesis, properties and solid state X-ray single crystal structures of two new rubrene-derivatives, viz diazarubrene (4,4'- (6,12-diphenyltetracene-5,11-diyl)dipyridine) and tetraazarubrene (5,6,11,12-tetra(pyridin-4-yl)tetracene) are reported. Both azarubrenes are more oxidatively stable than rubrene itself and show very similar optical properties but differ in their crystal packing from that of rubrene.

Rubrene (5,6,11,12-tetraphenyltetracene) is a benchmark semiconductor and has been studied extensively in the field of organic electronics.¹ So far, the highest reported holetransport mobility for rubrene has reached 40 cm²V⁻¹s⁻¹.² Also, rubrene promises powerful performance in next-generation solar cells with its high singlet fission quantum efficiency of nearly unity.³ Nevertheless, rubrene oxidizes easily in ambient surroundings,⁴ hampering its practical applications. Thus, various substituted rubrenes have been prepared and investigated. Douglas et. al. and Sakamoto et. al. have reported a variety of fluorinated rubrenes.⁵ The replacement of hydrogen atoms by electron-withdrawing fluorine atoms lowers the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, thus enhancing stability of rubrene against oxidation. Mamada and coworkers have developed and characterized a series of rubrene analogues with thienyl or furyl substituents,⁶ which showed increased photooxidation stability. However, to our knowledge, azarubrenes are unknown at the present. Introducing nitrogen atoms into π -system to form pyridine-like species stabilizes the frontier molecular orbitals of molecules and potentially convert parent hydrocarbon structures from p-type to n-type heterocyclic semiconductors.^{7,8} Therefore, we designed and synthesized two novel azarubrenes by introducing nitrogen atoms into the phenyl peripheries of rubrene.



Scheme 1. Synthetic route to Diazarubrene (DAR). *i*) K₂CO₃, THF/ CH₃OH = 1:1, room temperature (r.t.), 30 min; *ii*) benzophenone, *n*-BuLi, THF, 0 $^{\circ}$ C to r.t., 12 h; *iii*) methanesulfonyl chloride, triethylamine, 1,1,2,2-tetrachloroethane, 146 $^{\circ}$ C, 12 h; iv) O₂, dichloromethane, r.t., 5 d.



 $[\]label{eq:scheme 2. Synthetic route to tetraazarubrene (TAR). i) 4-Pyridinylboronic acid; Pd_2dba_3, Xphos, K_3PO_4, 1,4-dioxane, 100 <math display="inline">^\circ\!C$, 72 h; ii) O_2 , dichloromethane, r.t., 5 d.

The classic one-pot approach to rubrene using the allene protocol has been applied extensively. Some new derivatives of rubrene, such as 5,11-bis(3-thienyl)-6,12-diphenyltetracene and 5,11-bis(4-cyanophenyl)-6,12-diphenyltetracene, have been synthesized using this approach.⁹ To access **DAR** (Scheme 1) we prepared the carbinol 2. However, mesylation followed by heating in *o*-xylene to synthesize **DAR** from 2, using the allene method failed.

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Table 1. Photophysical, experimental and calculated electrochemical properties of rubrene, DAR, and TAR

Comp.	Abs _{max} ^[a] (nm)	Ems _{max} ^[a] (nm)	E _{ox} ^[b] (V)	E _{red} ^[b] (V)	HOMO (eV) mes. ^[c] /cal. ^[d]	LUMO (eV) mes. ^[c] /cal. ^[d]	gap (eV) mes. ^[e] /cal. ^[d]
rubrene	527	556	0.37 ^[f]	- 2.11 ^[f]	- 5.17/- 4.95	- 2.69/- 2.52	2.48/2.43
DAR	525	558	0.54 ^[f]	$-1.98^{[f]}$	- 5.34/- 5.24	- 2.82/-2.82	2.52/2.42
TAR	525	561	0.71 ^[g]	- 1.73 ^[f]	- 5.51/- 5.54	- 3.07/-3.13	2.44/2.41

[a] Absorption peaks and maximum emissions in dichloromethane. [b] Oxidation and reduction potentials measured in CV using ferrocene/ferrocenium as the reference redox system and internal standard (-4.8 eV). [c] Calculated from CV measurements ($E_{HOMO} = -4.80 \text{ eV} - E_{ox}$ (0/+); $E_{LUMO} = -4.80 \text{ eV} - E_{red}$ (0/-)). [d] Calculated by Gaussian 09 B3LYP/6-311++G**//BP86/def2-TZVP. [e] Estimated from E_{HOMO} and $E_{LUMO} - E_{HOMO}$). [f] Calculated from half-wave potentials. [g] Calculated from anodic peak potential.

Fortunately, when 1,1,2,2-tetrachloroethane was used as solvent, DAR was obtained in fairly poor yield of 14%. The simplicity of the synthesis renders the yield acceptable, but unfortunately this scheme did not work for TAR, so an alternative route was developed, starting from literature known tetrachlorotetracene 3.¹⁰ 3 had been employed to synthesize thienyl and furyl substituted rubrene derivates by Stille coupling. From 3, TAR was easily obtained by the coupling of **3** to 4-pyridinylboronic acid, through a fairly efficient Suzuki reaction, employing a Buchwald-type catalyst.¹¹ The desired TAR forms in 48% after column chromatography. Interestingly, in previous work, Douglas et. al. found that the reaction of **3** and phenyl magnesium bromide by Kumada-Tamao-Corriu cross-coupling undergoes an indene annulation reaction.¹² However, similar types of transformation do not occur under our conditions. Introducing more nitrogen atoms by coupling of 3 with substituted pyrimidines was not successful, using the above-developed conditions.



Figure 1. Normalized absorption and emission spectra of rubrene, DAR and TAR measured in dichloromethane.



Figure 2. Normalized time-dependent emission spectra of rubrene, DAR and TAR measured in dichloromethane.

As shown in Figure 1, DAR and TAR exhibit absorption and emission spectra similar to each other and to those of rubrene; this result is expected, as the chromophore, tetracene, is identical in all cases. Despite the presence of two or four nitrogen atoms in the periphery, DAR and TAR are still easily oxidized in air into DARO2 and TARO2; both emit blue-shifted, as expected by the breakup of the tetracene system (see Figure S1 in Electronic Supplementary Information, ESI).

Figure 2 shows a comparison of fluorescence intensity for solutions of rubrene, DAR, and TAR as a function of time in ambient air. After 24 h, the fluorescence intensity of rubrene, DAR and TAR have decreased by 52%, 24%, and 10% respectively. Both DAR and TAR therefore are considerably less sensitive towards oxidation in solution, but by no means air-stable for prolonged periods of time.

We were able to grow single crystals for XRD analysis of all of the four products, i.e. the azarubrenes but also their oxidized products. Single crystals of DAR, DARO2, and TARO2 were obtained by slow evaporation of saturated solutions of dichloromethane under ambient surroundings; TAR single crystals were grown successfully by slow evaporation of a THF solution in the glovebox. Rubrene displays three different polymorphs, orthorhombic (a = 26.78 Å, b = 7.17 Å, c = 14.26 Å), monoclinic (a = 8.74 Å, b = 10.13 Å, c = 15.64 Å, β = 91°), and triclinic (a = 7.02 Å, b = 8.54 Å, c = 11.95 Å, α = 93°, $\beta = 106^{\circ}, \gamma = 96^{\circ}$).¹³ As shown in **Table 2, DAR** (a = 7.07 Å, b = 8.27 Å, c = 11.86 Å, α = 90°, β = 106°, γ = 98°) crystallizes in the triclinic crystal system and its molecular packing (Figure 3a and **3e**) is close to isomorphous to that of triclinic rubrene crystals, grown by the solvent diffusion method. Both of them exhibit a planar tetracene backbone with slanted stacks. Noticeably, **DAR** exhibits a π - π stacking distance of 3.6 Å (0.2 Å shorter than that of rubrene¹³), a long-axis displacement of 6.1 Å, and the absence of short-axis displacement along crystal a direction (see Figure 3e and Figure S2 in ESI), indicating it might have more efficient cofacial π -stack interactions and electronic couplings than rubrene.¹⁴ This is further supported by Hirshfeld surface analysis¹⁵ (Figure 3g,h): Similar to triclinic rubrene,¹⁶ the main feature is a large, light blue colored region corresponding to π -stacking of the tetracene core. However, red regions on d_{norm} result exclusively from C-H··· π close contacts - H···H close contacts are less prominent and N···H close contacts contribute only 5.4% to the total surface area.

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Comp.	crystal system	space group	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	V (Å ³)
Rubrene ^[a]	triclinic	P Ī	7.02	8.54	11.95	93	106	96	684
DAR	triclinic	ΡĪ	7.07	8.27	11.86	90	106	98	660
TAR	triclinic	ΡĪ	7.76	18.66	21.77	98	90	101	3068

[a] The data of triclinic rubrene crystal is reported by Huang et al.¹²



Figure 3. Different views of single crystal structures of DAR (a), TAR (b), DARO2 (c), and TARO2 (d). Visualization of overlap and packing of DAR (e) and TAR (f). THF molecules are omitted for clarity in the TAR crystal structures. g) d_{norm} Hirshfeld surface for DAR. h) Fingerprint plot for DAR.

More interesting is the structure and the packing of triclinic **TAR** (**Table 2**). Contrary to **DAR**, the tetracene nucleus is somewhat twisted in this structure. Unfortunately, the compound crystallizes as a solvate and THF is part of the structure. As a consequence, the packing of the molecules is not rubrene-like anymore, and there is no appreciable overlap of the π -systems of different molecules. Attempts to grow

single crystals from other solvents only led to very small crystals.

We could also obtain specimen of the oxidized species, which are, as expected, the oxygen adducts formed through a formal 4+2-cycloaddition of **DAR** or **TAR** with O_2 . The molecular packing of these species is complicated (see **Figure S3** in **ESI**).

Quantum chemical calculations show the influence of the pyridine units on the energetic position of HOMO and LUMO. (Figure 4) Optimized geometries of rubrene, DAR and TAR are twisted as reported for rubrene.¹⁷ The FMOs are stabilized by 0.3 eV (DAR) and 0.6 eV (TAR) each in comparison to rubrene, pointing to an effect of around 0.15 eV per nitrogen atom, fairly additive.

In this work, we have introduced two or four pyridine substituents to rubrene and have modulated its frontier orbital positions, without touching the tetracene unit, working on the peripheral aromatic substituents. While this concept is not new, pyridine-substituted rubrenes have to our knowledge never been prepared and **3** is a versatile starting material for the introduction of different substituents to rubrene. In future we will exploit this concept further and introduce other electron accepting substituents into the rubrene core and investigate their structure, optical and electronic properties with the final goal to develop a high mobility n-channel-material based on the rubrene framework.

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Conflicts of interest

There are no conflicts to declare.

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