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11,11,12,12-Tetracyano-4,5-pyrenoquinodimethanes: Air-Stable Push–Pull *o*-Quinodimethanes with S_2 Fluorescence

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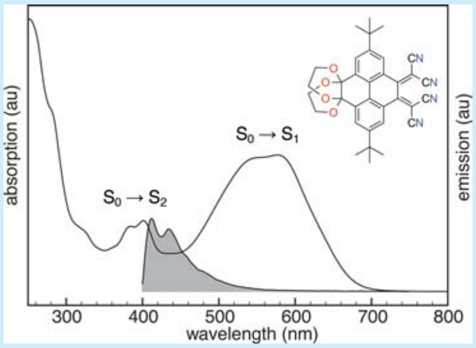
Supporting Information

ABSTRACT: The synthesis and properties of 11,11,12,12-tetracyano-4,5-pyrenoquinodimethanes (4,5-TCNPs), a new family of isolable and air-stable *o*-quinodimethanes, are reported. The *ortho* disposition of the dicyanomethane substituents strongly polarizes the pyrene framework to promote broad and intense intramolecular charge-transfer transitions. In addition, spectroscopic studies reveal that 4,5-TCNPs violate Kasha's rule and emit from the S_2 level.



The discovery of the strong electron affinity of 1,1,2,2-tetracyanoethylene (TCNE)[1] opened the door to the exploration of molecular materials in which four cyano groups are interconnected through a conjugated system. Among these, 7,7,8,8-tetracyano-1,4-quinodimethane (TCNQ) derivatives[2] have been the most popular by far. Partial charge transfer in co-crystals of TCNQ with electron donors provide organic metals.[3] Also, TCNQ covalently bound to electron donors provides push–pull and mixed valence compounds with charge-transfer character and magnetic properties.[4] This success has stimulated the synthesis and study of numerous tetracyanoquinodimethane derivatives, such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-1,4-quinodimethane (TCNQF4),[5] 11,11,12,12-tetracyano-2,6-naphtoquinodimethane (TNAP),[6] and 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ),[7] 11,11,12,12-tetracyanopyrenoquinodimethane (TCNP),[8] among others,[9] which offer a spectrum of varying electron affinities.

Among all the possible substitution patterns in tetracyanoquinodimethanes,[3f,10] there are no reported syntheses of derivatives with an *ortho* substitution, except for 11,11,12,12-tetracyano-2,3-(2,3,5,10-tetrahydro-5,10-dimethyl)phenazinoquinodimethane,[11] which was described as an unexpected cycloaddition product of TCNE. This is because *o*-quinodimethanes (*o*QDM) are very reactive and short-lived species[12] that have been detected in frozen rigid glass matrices[13] and just a few members embedded in a hydrocarbon frame have been isolated at room temperature.[11,14]

Herein, we report the synthesis and properties of 11,11,12,12-tetracyano-4,5-pyrenoquinodimethanes (4,5-TCNP) **1** and **2** (Scheme 1), a new family of isolable and air-stable *o*QDM. The *ortho* disposition of the dicyanomethane substituents strongly polarizes the pyrene framework to promote broad and intense (log ε = 3.64) intramolecular charge-transfer (ICT) transitions without the need of any electron-donating substituents. The introduction of electron-donating diketal through a novel methodology to desymmetrise pyrene promotes a more intense (log ε = 4.29) and broad ICT transition that covers almost entirely the visible part of the electromagnetic spectrum. In addition, spectroscopic studies reveal that solutions of **1** and **2** violate Kasha's rule[15] and emit from the S_2 level.

The synthesis of **1** and **2** was achieved following the route depicted in Scheme 1. Full details about the synthesis and characterization are given in the Supporting Information. Pyrene diketone **3** was obtained in two steps following a procedure reported by Harris.[16] Knoevenagel condensation of malononitrile with diketone **3** in the presence of $TiCl_4$ led to **1** in moderate yields (16%). In order to assemble the donor and the acceptor units along the K positions (4,5,9,10) and enhance the polarization, we have also developed a new synthetic strategy to desymmetrize pyrene. First, the ketones of **3** were transformed into diketal-protected **4** with an excess of ethylene glycol and a catalytic amount of *p*-toluenesulfonic acid (PTSA) in refluxing *o*-dichlorobenzene (ODCB), and water was removed by means of a Dean–Stark apparatus. Then the positions 9,10 of the resulting protected diketone **5** were subsequently oxidized to provide the asymmetric pyrene diketone **5**. In a similar fashion, diketone **5** also underwent

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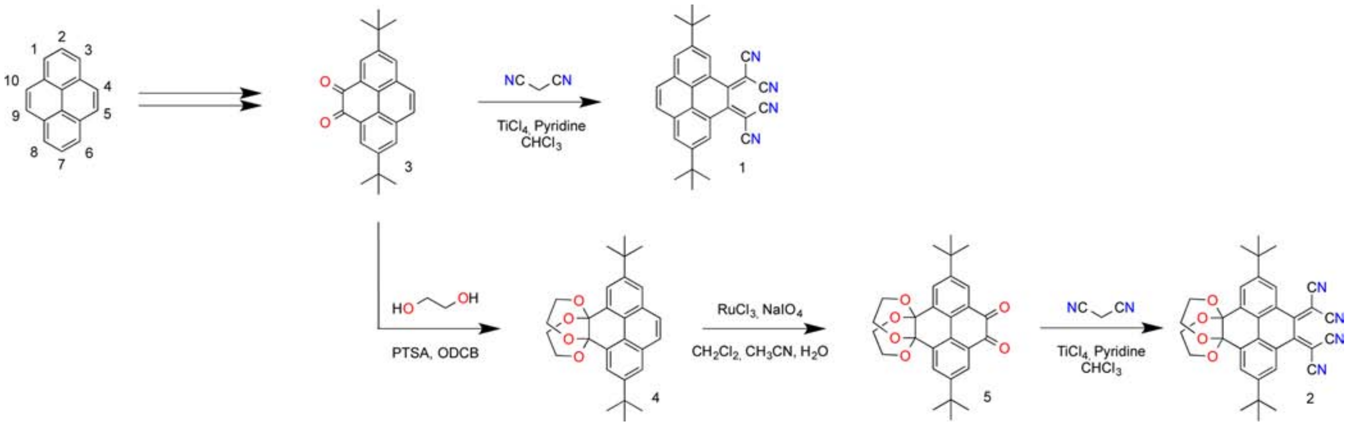
Scheme 1. Synthesis of 1 and 2



Knoevenagel condensation with malononitrile in the presence of $TiCl_4$ to provide **2** in low yields (8%). Both **1** and **2** are soluble in CH_2Cl_2, and $CHCl_3$ and THF and were characterized by NMR (^{1}H and ^{13}C) and MS.

The DFT-calculated structures of **1** and **2** (B3LYP 6-31G**) reveal a twisted structure due to the steric hindrance of the dicyanomethane groups in the *ortho* positions (Figure 1). Only one conformation was obtained for **1** regardless of the starting point. Conversely, two minima were obtained for **2** that are 6 kcal/mol apart and that differ on the conformation of the diketal (more stable conformer shown in Figure 1). The different conformations as a function of the *tert*-butyl groups yield negligible energy differences (<1 kcal/mol). The calculated structures are in good agreement with the X-ray structural data of 11,11,12,12-tetracyano-2,3-(2,3,5,10-tetrahydro-5,10-dimethylphenazino)quinodimethane[11] and of the diketal of pyrene-4,5-diketone (see compound **S1** in the Supporting Information).

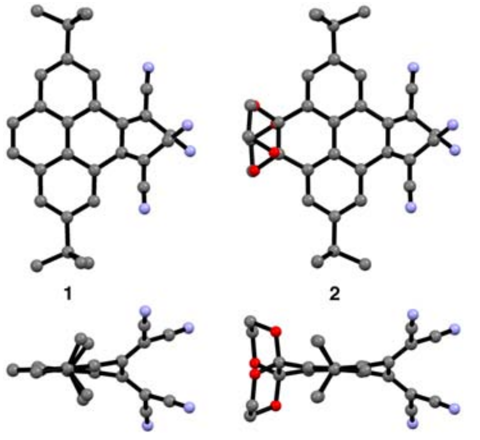


Figure 1. Front (top) and side (bottom) views of DFT (B3LYP 631G**)-minimized structures of **1** and **2** (C = gray, N = blue, O = red). Hydrogen atoms have been removed for clarity.

Compounds **1** and **2** are intensely colored, orange and purple, respectively. The absorption spectra of **1** (Figure 2) display a broad absorption band centered at 498 nm (log ε = 3.64) consistent with an ICT process that was assigned to a $S_0 \rightarrow S_1$ transition. Also, a well-resolved absorption band is discernible for **1** in the UV with clear vibronic features with maxima at 338 and 357 nm, which was assigned to a $S_0 \rightarrow S_2$ transition. In the case of **2**, the $S_0 \rightarrow S_1$ band is more intense (log ε = 4.29) and strongly red-shifted (79 nm) in comparison to **1** and shows vibronic features with maxima at 548 and 577 nm (Figure 2). This broad absorption is also consistent with an ICT transition. An additional absorption band is also discernible in the UV for **2** that is substantially red-shifted (44 nm) in comparison to **1**, which shows vibronic features with maxima at 382 and 401 nm. Similarly, this band was assigned to a $S_0 \rightarrow S_2$ transition. The S_0–S_1 energy gaps of **1** and **2** were estimated from the absorption onsets and correspond to 2.13 and 1.70 eV, respectively (see Table S1, Supporting Information). Such values reflect that the presence of the electron donors lowers the band gap substantially as an effect of the enhanced ICT character.

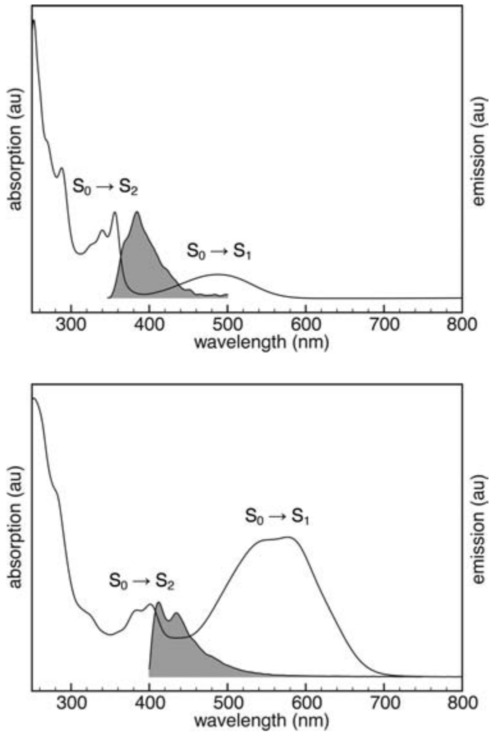


Figure 2. Absorption (white) and emission (gray) features for **1** (top) and **2** (bottom) in CH_2Cl_2.

The lowest energy singlet excited states were calculated using time-dependent density functional theory (TDDFT B3LYP 631G**) in order to shed light on the nature of the electronic transitions that give rise to the absorption bands in the electronic spectra (see the Supporting Information). TD-DFT predicts that the $S_0 \rightarrow S_1$ transition centered at 498 nm in **1** is described as a one-electron HOMO → LUMO transition with a HOMO-1 → LUMO contribution. The electronic distribution in the HOMO and in the HOMO-1 is mostly localized in the pyrene moiety, while the LUMO shows larger densities in the dicyanomethane groups, and consequently, the $S_0 \rightarrow S_1$ excitation implies ICT (Figure S3, Supporting Information). The $S_0 \rightarrow S_2$ band centered at 357 nm corresponds to a one-electron HOMO-2 → LUMO transition with a HOMO-1 → LUMO contribution. The picture is slightly different for **2**, where the $S_0 \rightarrow S_1$ band centered at 577 nm corresponds to a HOMO → LUMO transition. The electronic distribution in the HOMO is again more localized in the pyrene moiety while the LUMO shows larger densities in the dicyanomethane groups, and thus, the $S_0 \rightarrow S_1$ excitation also implies ICT. The $S_0 \rightarrow S_2$ band centered at 401 nm is described as a one-electron HOMO-2 → LUMO transition with a HOMO-1 → LUMO contribution.

Fluorescence studies carried out on **1** and **2** (Figure 2) reveal that no emission is obtained upon excitation from the lowest energy $S_0 \rightarrow S_1$ band. Importantly, emissions with clear vibronic features were obtained upon excitation of the corresponding $S_0 \rightarrow S_2$ transitions. Such emission bands are centered at 384 and 411 nm, respectively, for **1** and **2**, which correlate in energy with a radiative $S_2 \rightarrow S_0$ deactivation since they are almost mirror images of the $S_0 \rightarrow S_2$ band. According to Kasha's rule,[15] *the emitting electronic level of a given multiplicity is the lowest excited level of that multiplicity*. The fact that compounds **1** and **2** violate Kasha's rule can be attributed to the large S_1–S_2 energy gap that favors emission from S_2 rather than nonradiative internal conversion (IC) as an effect of the diminished overlap between vibrational levels of S_1 and S_2. Taking into account the size of the S_1–S_2 energy gap (0.825 eV) for zinc 5,10,15,20-tetraphenylporphyrin (ZnTPP),[17] which is among the molecules that emit from the S_2 level,[17e,18] it is reasonable to think that the larger S_1–S_2 energy gaps[19] of **1** and **2** (0.98 and 0.94 eV, respectively) lead to a violation of Kasha's rule and thus to the emission from the S_2 level.

The redox properties of **1** and **2** were examined by cyclic voltammetry, which reflects their strong electron affinity (Figure 3). Remarkably, **1** and **2** preserve the reversible cathodic electrochemistry of tetracyanoquinodimethanes. The voltammograms of **1** shows two one-electron reversible reduction waves at low reduction potentials ($E_{1/2}$ = −0.21 and −0.40 V vs SCE) corresponding to the radical anion and the dianion, respectively. On the other hand, a one reversible two-electron[20] reduction wave ($E_{1/2}$ = −0.34 V vs SCE) was observed for **2** (SCE = saturated calomel electrode). In both cases, no oxidations were observed in the anodic scans within the solvent/electrolyte window. Although different, the electrochemical behavior of **1** and **2** is consistent with that of other tetracyanoquinodimethanes such as TCNQ ($E_{1/2}$ = −0.12 and −0.72 V vs SCE)[21] and TCAQ ($E_{1/2}$ = −0.70 V vs SCE)[21] in which dicyanomethanes are also reduced in two one-electron reduction processes and in a single two-electron reduction process, respectively. The LUMO levels were estimated from the potential onsets of the first reduction waves. The E_{LUMO} for **1** and **2** correspond to −4.18 and −4.05 eV, respectively. Even if the LUMO level of **2** is slightly higher in energy than that of **1**, remarkably, the electron affinity of **2** is maintained even in the presence of the diketal electron-donating groups, which illustrates the high electron-accepting power of the dicyanomethane groups in the *ortho* positions.

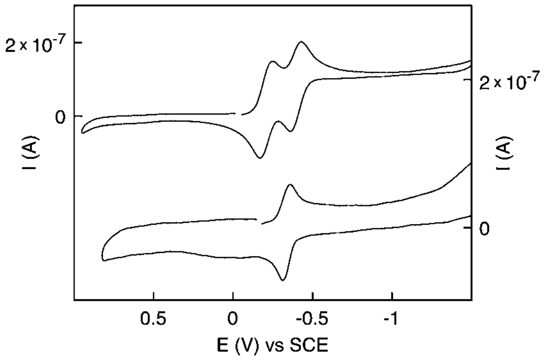


Figure 3. Cyclic voltammograms of **1** (top) and **2** (bottom) in 0.1 M n-Bu_4PF_6/THF.

In summary, we have reported a methodology to synthesize a new family of isolable and air-stable *o*QDM, namely 4,5-TCNPs. The *ortho* disposition of the dicyanomethane groups strongly polarizes the pyrene framework, promoting ICT transitions even without electron-donating substituents. In the presence of diketal electron donors—introduced through a novel methodology to desymmetrize pyrene—such ICT transitions become more intense, broadened, and red-shifted to almost entirely cover the visible part of the electromagnetic spectrum. In addition, 4,5-TCNPs violate Kasha's rule and emit from the S_2 excited state. Remarkably, 4,5-TCNPs preserve the reversible cathodic electrochemistry of tetracyanoquinodimethanes, including a very high electron affinity (E_{LUMO} = ∼ −4.1 eV). The combination of these properties makes 4,5-TCNPs ideal candidates to develop new optoelectronic materials for applications in fields in which tetracyanoquinodimethanes have been typically used, such as photovoltaics and nonlinear optics, as well as in new fields currently under exploration.[22]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details on synthesis and characterization of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) Estimated from the bands' maxima as there is an overlap between the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ bands.

(20) Estimated in the presence of an equimolar amount of ferrocene as internal standard.

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