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Solvent-Responsive Radical Dimers

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Abstract

An air- and thermally stable aryl dicyanomethyl radical is reported that switches between two dimeric forms—a σ dimer and a π dimer—by changing the solvent. The two dimer forms exhibit unique optical properties leading to solvatochromic behavior. The solvent-responsive behavior of these radicals can be explained by the higher polarizability of the π dimer than the σ dimer that leads to π dimer stabilization in polar solvents.

Disciplines

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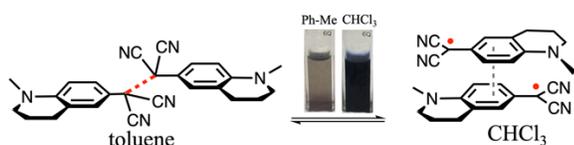
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Solvent-Responsive Radical Dimers

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Supporting Information Placeholder



ABSTRACT: An air- and thermally-stable aryl dicyanomethyl radical is reported that switches between two dimeric forms—a sigma dimer and a pi dimer—by changing the solvent. The two dimer forms exhibit unique optical properties leading to solvatochromic behavior. The solvent-responsive behavior of these radicals can be explained by the higher polarizability of the pimer than the sigma dimer that leads to pimer stabilization in polar solvents.

Materials that change properties in response to an environmental cue or an external stimulus are less commercialized than static materials but are needed to make new materials that can dynamically change their properties.¹⁻³ These dynamic materials have potential applications in self-healing plastics, glues with switchable adhesion, environmentally-responsive coatings and surfaces, switchable catalysts, chemical sensors, dynamic fabrics, and chemical actuators with switchable conductivity and magnetism.

A traditional approach for achieving dynamic synthetic materials involves the construction of materials that break and reform covalent bonds upon application of a stimulus, leading to a change in the structure of the material and accompanying property changes. A common drawback with this approach is that breaking normal covalent bonds sometimes requires harsh stimuli or causes irreversible changes to the material. In the ideal case, the stimuli-responsive material teeters on the knife-edge between two or more interconvertible forms with widely different properties, so that a small change in the environmental conditions nudges the structure from one form to another with large accompanying changes in the properties.

Here we examine a variant of the strategy of breaking and reforming bonds upon a stimulus, but with a change from standard covalent bonds to weak bonds. This goal is accomplished by using air- and thermally-stable aryl dicyanomethyl radicals

that exist in equilibrium with weakly-bonded sigma and pi dimers (pimers), with each dimeric form having differing properties. Sigma dimers have properties that resemble normal organic molecules, while pimers exhibit properties that are unusual for typical organic structures. The unusual properties of these pimers (or ‘pancake dimers’⁴) can be explained by its multicenter covalent bonding motif that brings the atoms closer than the van der Waals distance but longer than typical two-atom bonds (>2.8 Å).⁵⁻⁷ Thus, while σ -dimers usually absorb mostly in the UV region of the optical spectrum and have properties that are more consistent with “normal” closed-shell organic molecules, pimers are typically colored species that absorb visible to near-infrared light and feature unusual conductive and magnetic properties.

Here, we demonstrate that by careful structural tuning, radicals can be made that exhibit environment-responsiveness, so that changing the solvent leads to a change in the structure of the dimer from a sigma dimer to a pimer, with accompanying changes in the properties.

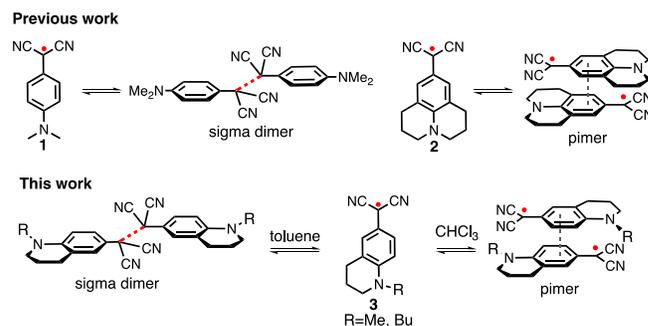


Figure 1. Radicals and modes of dimerization.

Previously, we demonstrated that an aryl dicyanomethyl radical with a p-dimethylamino substituent **1** forms a sigma dimer when cooled,¹⁰ while Seki and coworkers showed that a julolidine-derived radical **2** forms a pimer when cooled.⁵ Here, we show that the structural compromise of these two radicals, an alkyl tetrahydroquinoline-derived radical **3**, forms a sigma

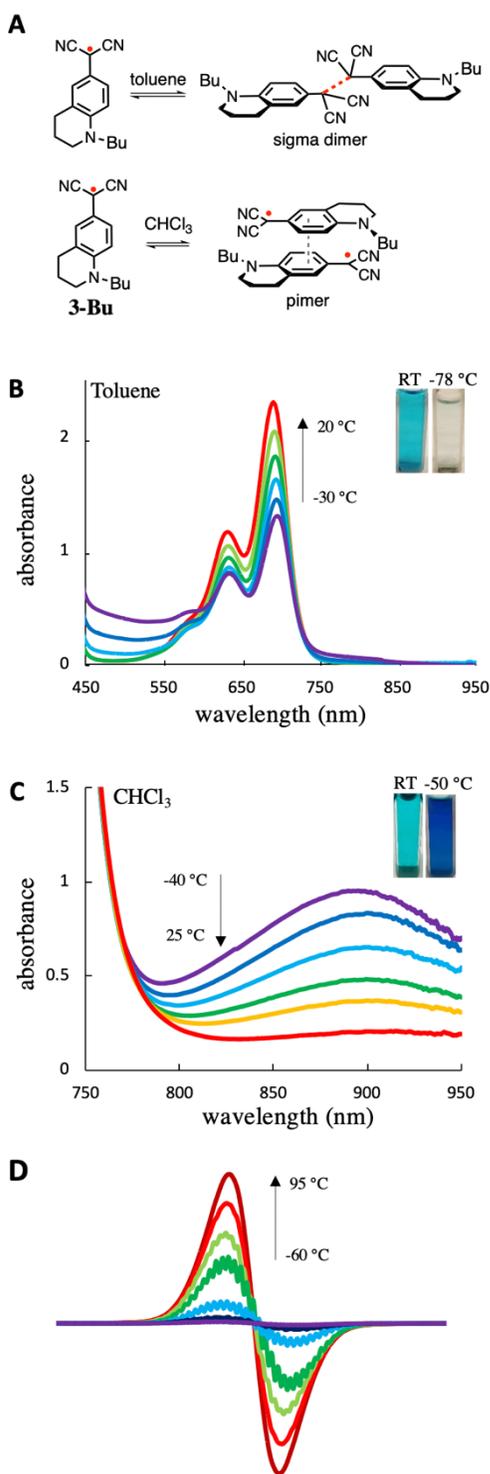


Figure 2. A. Modes of dimerization for **3**. B. Change in UV-Vis spectrum as a function of temperature in toluene. C. Change in UV-Vis spectrum as a function of temperature in CHCl_3 . Variable-temperature EPR for **3** showing loss of signal as solution is cooled.

dimer in toluene and a pimer in more polar solvents such as CHCl_3 . For this radical, the two dimeric forms are nearly degenerate and a small change in the environmental conditions can lead to a change in the preferred dimeric form, with a large change in the optical properties. In toluene, this sigma dimerization can be seen by a loss of the radical band in the visible

region of the optical spectrum upon cooling and the solution becoming colorless as the sigma dimer is formed. In contrast, in chloroform, **3** forms a pimer upon cooling, as observed by an increase in the visible radical band plus the emergence of the characteristic weakly-absorbing pimer band centered ~ 900 nm. In appearance, the solution of **3** at room temperature appears blue as a result of a thermal population of the colored free radicals, but turns clear upon cooling in toluene as the colorless sigma dimer is formed. In contrast, the radical **4** turns darker and purple upon cooling in chloroform as a result of the free radical pimerization. In all cases, upon cooling the EPR spectrum of the radical disappears indicating the formation of a diamagnetic species, which returns the same EPR spectrum upon warming (example shown in Figure 1D). This demonstrates that the dimeric form, including the pimer, has a singlet ground state.

The difference in solvent-responsiveness between radicals **1**, **3** and **4** can be seen more clearly in Figure 3, which shows the change in the optical properties of the radicals as a function of CHCl_3 /toluene solvent ratio. In the case of the dimethylamino-substituted radical **1**, at room temperature there is a thermal population of the blue-colored free radical in toluene. As the solvent ratio changes in favor of CHCl_3 , the free radical bands ~ 650 nm increase and the solution becomes darker blue as a result of a greater population of the free radical in the more polar solvent. The association constant for dimerization, K_a , determined from variable-temperature EPR and van'T Hoff plots for **1** is $2.0 \times 10^5 \text{ M}^{-1}$ in toluene, while in more polar DMF it is $2.5 \times 10^3 \text{ M}^{-1}$, indicating that as the solvent polarity is increased the radical is more favored in the equilibrium. A similar behavior is observed at -78°C , except that the amount of radical present is smaller. In both toluene and CHCl_3 , the sigma dimer is formed upon cooling.

In contrast, for radical **4**, at room temperature there is relatively little change as a function of solvent ratio. At low temperature, the pimer band ~ 900 nm is observed, and this band diminishes as the solvent features more CHCl_3 , indicating a larger population of free radical and less of the pimer in the more polar solvent. In both toluene and CHCl_3 , for radical **4** a pimer is observed.

In the most interesting case, **3**, at low temperatures a sigma dimer is formed in toluene, while as the solvent ratio is varied to the more polar CHCl_3 , the pimer band ~ 900 nm grows in and the solution becomes a dark purple, indicating a change in the mode of dimerization from sigma dimer to pimer in the more polar solvent (similar behavior is seen in toluene and acetone; see Supporting Information).

This solvent-responsive dimerization behavior can be explained by differences in polarizability between the sigma dimer and the free radicals and the diradical pimer. The free radicals themselves can be classified as captodative radicals, or radicals stabilized by both donor and acceptor substituents. Although the details remain controversial, captodative radicals¹¹ are thought to enjoy a special enhanced stability, which can be explained in the resonance model by the contribution of the zwitterionic structures shown in Figure 4A. Within polar solvents, solvent screening of these zwitterionic forms stabilizes the radical. This polarizability can be observed by the solvent-dependence of the strength of the radical association, which have larger association constants for dimerization in non-polar solvents than polar solvents. Additionally, the change in the electronic structure and increased contribution of the zwitterionic forms can be observed by the increase

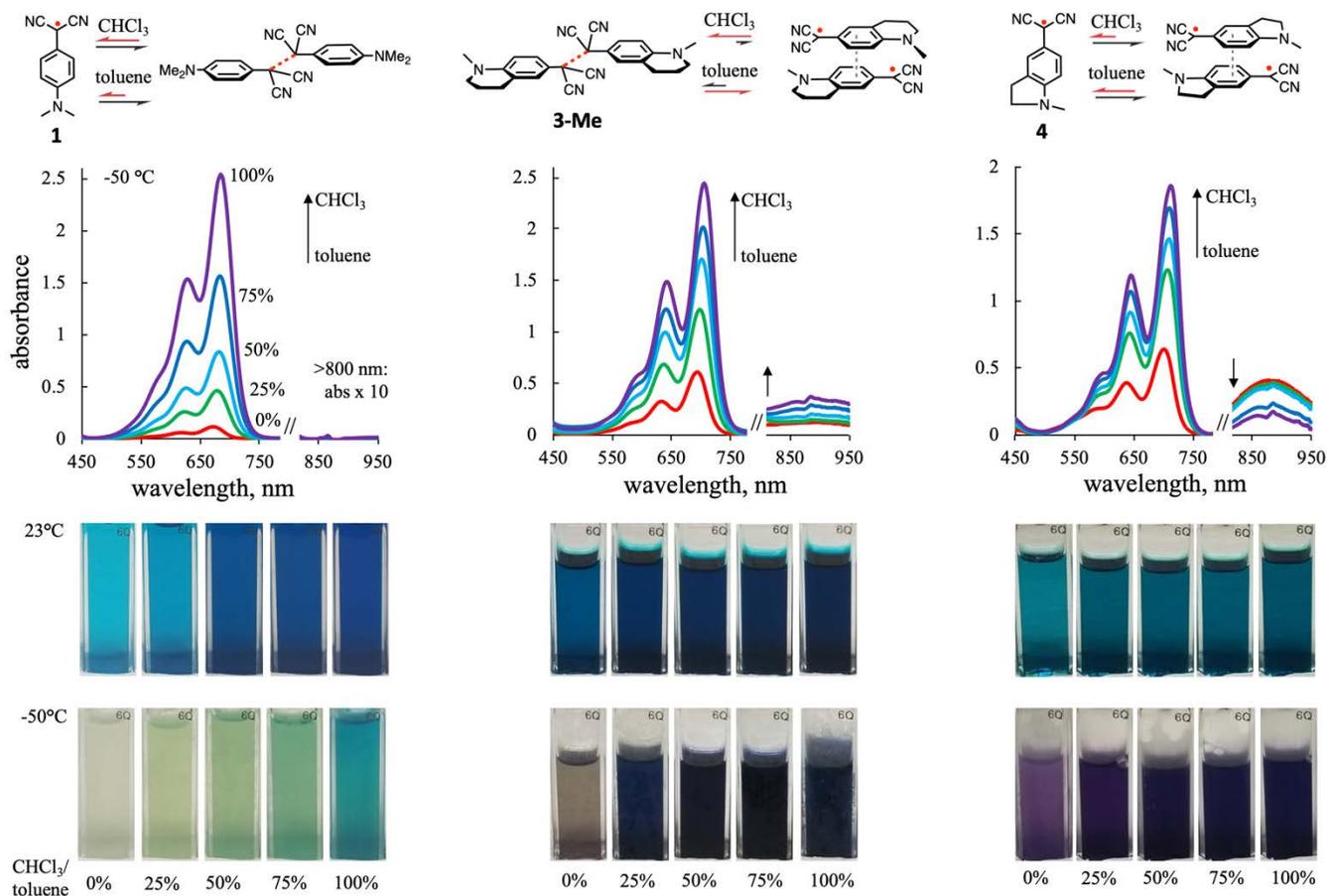


Figure 3. Top: Relevant equilibria for radicals **1**, **2** and **4**. Middle: UV-Vis spectrum as a function of solvent ratio (3 mM, all insets at >800 nm show absorbance multiplied by 10 to see the weak pimer band more clearly). Bottom: Photos of the solutions with varying toluene/CHCl₃ ratios at room temperature and -50 °C.

in the para-nitrogen EPR hyperfine coupling constant in polar solvents.⁸ As shown in Figure 4B, the calculated Mulliken spin densities show a decrease in the benzylic carbon spin density as the solvent dielectric is increased, with a concomitant increase in the spin density of the para nitrogen. Figure 4C shows the change in the computed spin densities between the SMD toluene solvation model and with an SMD water solvation model, which indicates the increased spin delocalization in polar solvents. Alabugin and coworkers have noted that highly polarizable diradicals is a manifestation of the diradical/zwitterion “two-faced”²⁰ character of these species.²¹

Computation also suggests that these pimers have considerable diradical character. Within DFT models, the singlet pimers are unstable with respect to an RHF→UHF perturbation. A broken-symmetry singlet DFT calculation is highly spin contaminated ($\langle S^2 \rangle > 0.75$) and suggests that these diradical pimers have considerable singlet diradical character, and the SOMOs show one radical mostly occupying one ring with the other radical mostly occupying the other.²² These highly spin-contaminated Kohn-Sham orbitals should be interpreted with caution, but suggest that the pimers contain free radical character despite the overlap of the pi SOMOs. Thus, if the radicals are stabilized by polar solvents, then the pimers, which also have radical character, should also be stabilized by polar solvents. Additionally, a crystal structure of the pimer of **2** shows that it adopts a head-to-tail geometry.⁵ If in polar solvents the radicals become more

polarized towards charge-separated structures, that could lead to electrostatic stabilization of the pimer (Figure 4E). Indeed, a computation of the sigma dimer—pimer relative electronic energies (UωB97DX/6-31+G(d,p), SMD) indicates that the sigma dimer is favored by 0.7 kcal/mol in the phase, but the pimer is favored in water by 4.1 kcal/mol.

Substituted aryl dicyanomethyl radicals were recently shown by Seki and coworkers,^{4,5} and subsequently by us⁶⁻⁸ and others⁹ to be air- and thermally-stable species that exist in a thermal equilibrium with dimers. When cooled, the radicals typically dimerize to form either a head-to-head sigma dimer with an elongated bond, or a pimer, depending on the substituents attached to the aromatic ring. Radicals with withdrawing groups or weakly donating groups tend to form sigma dimers while radicals with very strong donating groups can form pimers. Recent studies indicate that a combination of London dispersion forces, spin delocalization effects, and polarization play a role in directing whether a sigma dimer or a pi dimer is formed for these radicals,⁸ and have also shown that the radical is stabilized in polar solvents.⁷

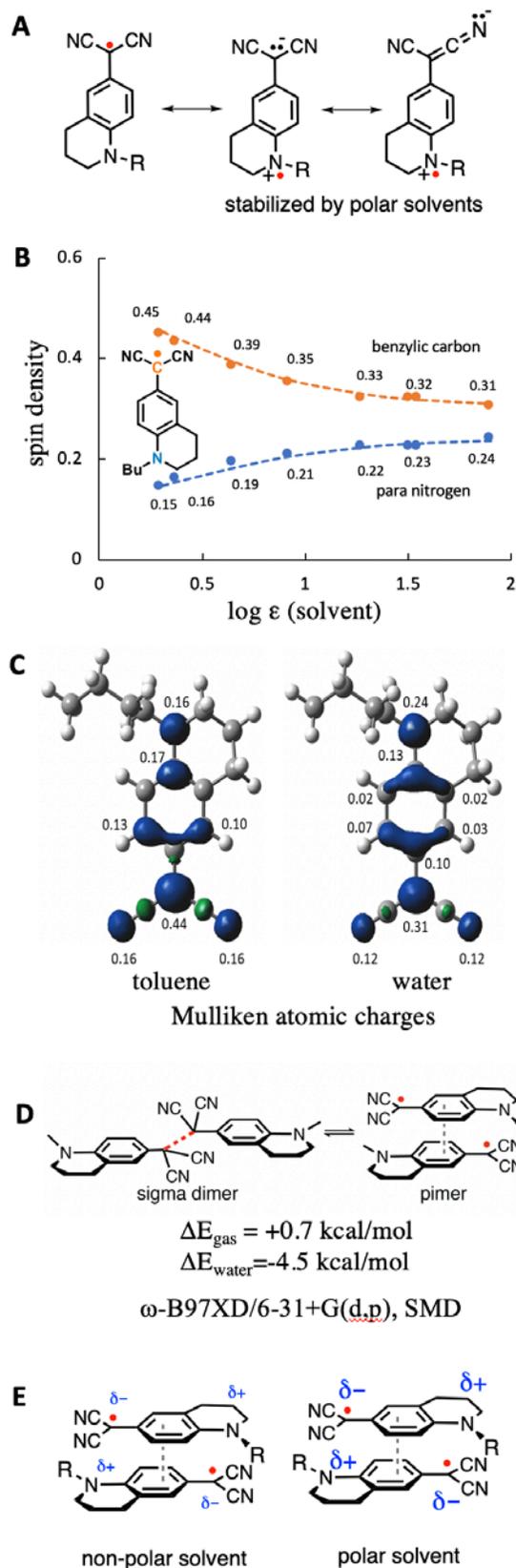


Figure 4. A. Captodative stabilization in the resonance model. B. Change in spin density as a function of solvent dielectric ($\omega\text{-B97XD/6-31+G(d,p)$, SMD). C. Change in computed Mulliken atomic charges for 3-Bu in toluene and water ($\omega\text{-B97XD/6-31+G(d,p)$, SMD). D. Computed equilibrium energetics ($\omega\text{-B97XD/6-31+G(d,p)$, SMD). E. Polarization model for stabilization of the pimer in polar solvents.

In conclusion, we have identified a radical that can change modes of dimerization from sigma to pi dimer based on its solvation environment. The polarizability of the pimer causes it to be stabilized in polar solvents in preference to the less polarizable sigma dimer. Identifying this solvent-responsive radical requires walking a structural tightrope, as slight structural variants do not exhibit this stimuli-responsive behavior. Potentially, this radical may be incorporated as a building block into polymeric materials that achieve stimuli-responsiveness, and also holds promise for use in sensors that exploit the unique conducting and optical properties of the pimer as the readout.

ASSOCIATED CONTENT

Supporting Information. Computational coordinates and absolute energies. Data and pictures of the radicals solvent-responsiveness with different solvent combinations. The Supporting Information is available free of charge on the ACS Publications website.

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