Fluorescence Depolarization in Molecular Gyroscopes: Evidence of a Photonic Brake.

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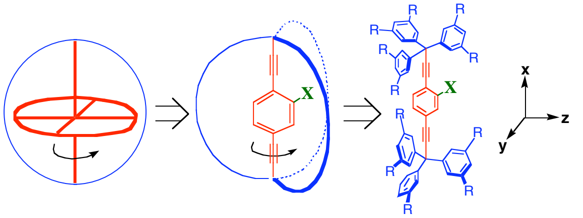
We recently reported the design, construction, and dynamics of crystalline solids built with molecules having structures and properties analogous to those of macroscopic compasses and gyroscopes.[1] As illustrated in Scheme 1, they consist of a 1,4-diethynylbenzene linked to triarylmethanes[1] or triptycenes.[2]

Scheme 1



1a) R=X=H
1b) R=*tert*-Bu, X=H
2) R=H, X=F
3) R=H, X=CN

Our interest in molecular compasses and gyroscopes stems from their potential in the fabrication of ultrafast electro-optic materials.[3] Ideally, the response of their reorienting dipoles to external fields should result in tunable birefringence, dichroism, and nonlinear optical effects. Indeed, rotation about alkyne-aryl sigma bonds is known to be barrierless in the gas phase,[4] and examples of such bonds in crystals with ground-state rotational time constants of less than 100 ns at 300K (*e.g.*, **1b**)[1c] bode well for the construction of nearly frictionless rotating units in solids.

In an attempt to measure their gyroscopic motion in their lowest electronic excited state, we decided to explore the fluorescence depolarization of the molecules in Scheme 1 in solution with the hope of extending later to the solid state. The idea was to directly measure the rotational diffusion of the central phenylene group by exciting the molecule with polarized light, and collecting the emission from a state whose transition dipole has a component perpendicular to the alkyne bonds (along the *z*-axis in Scheme 1).[5] However, instead of a rapid depolarization consistent with rotation of the central phenylene, we observed a much slower process consistent with rotation of the entire molecule. Based on this and known changes in the excited-state bond order,[6] we propose that electronic excitation causes a stoppage of the gyroscopic rotation about the original alkyne-arene single bonds in what can be thought of as a "photonic brake".[7]

To analyze the rotational correlation times, experiments were carried out with 10^{-5} M solutions in solvents of different viscosity: methyl cyclohexane (MCH), CH_2Cl_2 and mineral oil.[8] The UV-Vis and fluorescence spectra of compounds **1a** and **2** are essentially identical to those of the corresponding 1,4-diethynylarenes.[9] It has been suggested that the weak fluorescence of *p*-diethynylbenzene results from mixing the symmetry-allowed S_2 ($^1B_{1u}$) state mwith a small amount of the symmetry-forbidden S_1 ($^1B_{2u}$) state.[10] The main effect of the -F and -CN substituents is to add oscillator strength to the otherwise forbidden S_1 transition and to increase the fluorescence quantum yield and lifetime in CH_2Cl_2 from $\square_F$=0.05 and $\square_F$=0.32 ns in **1a** to $\square_F$=0.44 and $\square_F$=1.6 ns in **3** (see Table 1). The emission maxima of **1a**, **2**, and **3** occur at 315, 317, and 339 nm, respectively. Our hope was that the substituents would cause the transition dipoles of **2** and **3** to lie closer to the *z*-axis than that of compound **1a**. However, what we will see below is that the emission dipole moments of all three molecules are rotated by ~24° with respect to the absorption dipole.

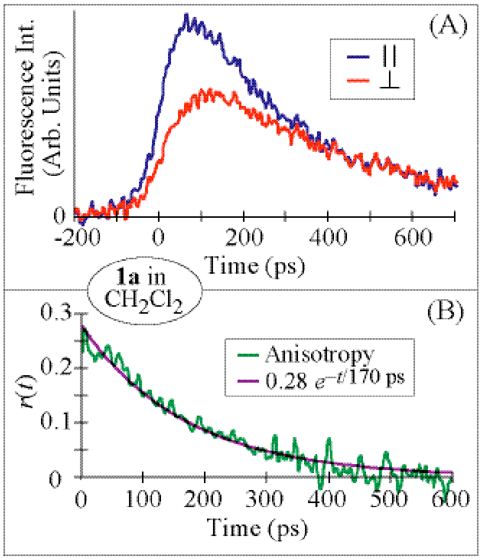


Figure 1. (Top) Fluorescence dynamics of **1a** following polarized excitation at 293 nm with excitation and detection polarized either parallel (blue) or perpendicular (red) to each other. (Bottom) Anisotropy decay (Eq. 1, green) and single-exponential fit (cyan).

Figure 1 shows the fluorescence depolarization of **1a** in CH_2Cl_2 at 292 K. Polarized excitation pulses of ~100 fs were tuned to the lowest energy absorption band ($\square$=293 nm). The emission, collected through a polarizer set either parallel (||) or perpendicular ($\square$) to the polarization of the excitation pulse, was imaged onto the cathode of a streak camera with ~10 ps resolution.[11] The fact that || emission is stronger than $\square$ emission indicates that the absorption and emission dipoles make an angle that lies between 0° and 54.7° (the magic angle). We calculated the fluorescence anisotropy dynamics using the time-resolved fluorescence data and eq. 1:

$$r(t) = \frac{\|(t)\,\square\square(t)}{\|(t) + 2\square(t)} \qquad \text{Eq. 1}$$

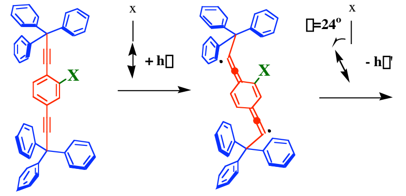
For all three molecules in all three solvents, the anisotropy decays fit cleanly to a single exponential, with an initial value of $r(0)$=0.28±0.05 (Table I); for example, the bottom panel

Table 1. Fluorescence lifetimes and anisotropy decay parameters from compounds **1a**, **2**, and **3**.[a]

		CH_2Cl_2 (η=0.44)[g]			MCH (η =0.74)[g]			Mineral Oil (η =29)[g]		
	Free Rotor	Lifetime	Anisotropy		Lifetime	Anisotropy		Lifetime	Anisotropy	
	τ_{FR} (ps)[e]	τ_F[b] (ns)	$r(0)$[c]	τ_A (ps)[b]	τ_F[b] (ns)	$r(0)$[c]	τ_A (ps)[b]	τ_F[b] (ns)	$r(0)$[c]	τ_A (ps)[b]
1a		0.32±0.05	0.27	170±20	0.64±0.05	0.22	250±50			
2					1.7±0.5	0.28	250±50			
3		1.6±0.15	0.28	180±20	2.1±0.2	0.28	220±30	2.1±0.2	0.23	>2500
Prolate rotor	6.5[e]			110[d]			185[d]			7250[d]
Gyroscope[f]	0.418[e,f]			26[d,f]			43[d,f]			192[d,f]

[a] No fast decay was observed within ~10 ps resolution. [b] Single exponential. [c] Error in r(0) is 0.05. [d] Values calculated with eq. 2. [e] Values calculated as in ref. 13. [f] Assuming the dimensions of diethynyl benzene. [g] Viscosities from reference 8.

Scheme 2



of Figure 1 shows that the anisotropy decay of **1a** in CH_2Cl_2 decays exponentially with a time constant τ_A=170±20 ps. The fact that the anisotropy decays fit well to single exponentials indicates that there is only one dominant rotational motion in the excited state. Initially this came as a surprise given that we expected a fast anisotropy decay due to the gyroscopic motion of the central phenylene unit, followed by slower decays resulting from rotational diffusion about the shorter and longer molecular axes of this prolate-spheroidal molecular top.

To better understand the observed anisotropy decays, we analyzed the effects of solvent viscosity on the kinetics of depolarization using a Stokes-Debye-Einstein model,[12]

$$\tau_{rot} = 4\pi\eta ab^2 fC / 3k_B T \qquad \text{Eq. 2}$$

where η is the solvent viscosity, a and b are the dimensions of the half molecular axes (a=8.3Å and b=4.6Å, derived from the X-ray structures[1b]), and the factors f=1.37 and C=+1, obtained from ref. 12, account for the prolate shape of the molecule and hydrodynamic stick boundary conditions, respectively. The expected rotation times for molecular reorientation of a prolate spheroid (calculated using Eq. 2) and the rate of gyroscopic motion by the central phenylene (assuming an ideal free rotor[13] in a frictionless medium) at 292 K are also included in Table 1.

Comparing the calculated and experimental rotation rates in Table 1 in the three solvents suggests that each of the anisotropy decays results from prolate rotation of the entire molecule. This requires that the emission dipole lie mainly along the main (x) molecular axis, consistent with the dominant $^1B_{1u}$ state character of the excited state.[10] Table 1 also shows that gyroscopic motion, if it occurred in the excited state, would have been easily detected within the ~10 ps time resolution of our measurements. Thus, we have strong evidence that photoexcitation causes gyroscopic motion to cease, providing a means for photonic braking.

Information concerning *why* photoexcitation leads to photonic braking can be found in the time-zero values of the anisotropy, $r(0)$, which are also summarized in Table 1. The observed value of $r(0)$=0.28 (instead of $r(0)$=0.4, the value expected for collinear dipoles) suggests either a depolarization mechanism that is faster than our time resolution or a significant rotation of the transition dipole for emission relative to that for absorption. Since the fastest rotational processes should be slower than our time resolution (Table 1), we prefer the latter possibility.

The fact that **2** and **3** give identical results (within experimental error) to **1a** confirms that there are no rotation processes that occur faster than our time resolution. The fact that $r(0)$=0.28 thus requires the emission dipole in all three molecules to be rotated by ~24° relative to the absorption dipole. A change of this type is what might be expected for an electronic excitation accompanied by strong vibronic coupling with in-plane deformation between the ring and the trityl groups, deformation of the acetylenic triple bond, and an in-plane ring deformation, as suggested by Laposa.[10a] In addition, well-known changes in bond order[6] suggest a bis-allenic excited state, as illustrated in Scheme 2. Put together, the results suggest that excitation of molecular compasses based on di-alkynylphenylene rotors arrest the free rotation of the ground state. Mechanisms such as these may become the basis of photonic braking in artificial molecular machines, allowing non-linear optical or other thermally activated gyroscopic processes to be switched off at will.

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