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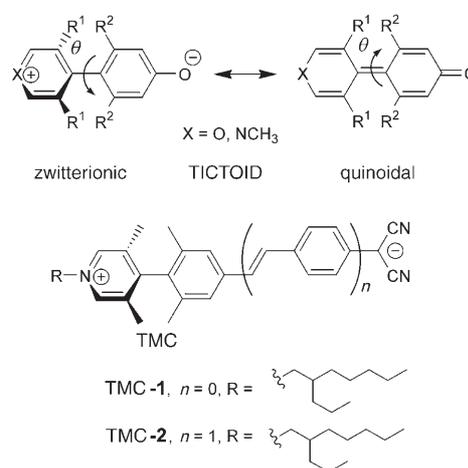
Exceptional Molecular Hyperpolarizabilities in Twisted  $\pi$ -Electron System Chromophores\*\*

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Molecule-based electrooptic (EO) materials are of intense research interest for understanding how light interacts with matter and for applications in photonic technologies such as high-speed optical communications, integrated optics, and optical data processing and storage.<sup>[1]</sup> In such materials, the second-order susceptibility tensor governing EO response ( $r_{33}$ ), is governed both by the net polar microstructural order and the microscopic molecular first hyperpolarizability tensor ( $\beta$ ). Large  $\beta$  values are essential for large EO response, and the quest for higher performance EO chromophores presents a daunting challenge.<sup>[1]</sup> To date, effective chromophores have been designed according to similar principles embodied in the classical “two-level” model: conjugated  $\pi$  systems end-capped with donor (D) and acceptor (A) moieties.<sup>[2]</sup> Elegant efforts have sought maximum  $\beta$  by optimizing D and A strengths and conjugation pathways,<sup>[3]</sup> directed by “bond length alternation”<sup>[4]</sup> and “auxiliary donor and acceptor” models.<sup>[5]</sup> Such strategies utilize extended *planar*  $\pi$ -conjugation, resulting in chromophores that are inherently elaborate

structurally, complicating synthesis and introducing potential chemical, thermal, and photochemical instabilities.<sup>[6]</sup> Alternative routes to very large- $\beta$  chromophores would clearly be desirable, and there is growing evidence that simple two-level systems may not provide access.<sup>[7]</sup>

Recent theoretical work suggests that unconventional chromophores with *twisted*  $\pi$ -electron systems bridging D and A substituents (TICTOID = twisted intramolecular charge-transfer; Scheme 1) may exhibit unprecedented hyperpolar-



Scheme 1. Structures of TICTOID and TMC (twisted  $\pi$ -electron system molecular chromophore).

izabilities through non-classical mechanisms.<sup>[8]</sup> These would have relatively simple biaryl structures in which  $\beta$  is sterically tunable through  $R^1$ ,  $R^2$  modification of the interplanar dihedral angle ( $\theta$ ). Large  $\beta$  magnitudes are predicted at  $\theta \approx 70$ – $85^\circ$ ,<sup>[8a]</sup> with twist-induced reduction in D- $\pi$ -A conjugation leading to charge-separated zwitterionic ground states. The intriguing question is whether such molecules, with small numbers of  $\pi$ -electrons, could thereby exhibit far larger  $\beta$  values than conventional planar chromophores.

We report here the first realization of such TICTOID chromophores, that they have unprecedented hyperpolarizabilities on the order of 10–20 $\times$  larger than previously observed,<sup>[1–5]</sup> and that these are not simple two-level systems. The new chromophores (Scheme 1) were designed according to the following criteria: 1) Synthetically challenging tetra-*ortho*-alkylbiaryl cores should enforce large interplanar angles, judging from bimesityl ( $\theta \approx 90^\circ$ ).<sup>[9]</sup> 2) Dicyanomethane and pyridinium groups should be effective D and A substituents, with dicyanomethane more stable than phenoxide.<sup>[10]</sup> 3) Pyridine alkylations should enhance solubility and processability (TMC-1 and TMC-2), with styrenic substitution further enhancing  $\beta$  (TMC-2).

TMC syntheses (Scheme 2) begin with precursor **1**, synthesized as reported elsewhere.<sup>[10]</sup> Pd-catalyzed NaCH(CN)<sub>2</sub> coupling affords **2**, which is then regioselectively quaternized<sup>[11]</sup> and deprotonated to afford TMC-1. Precursor **3** is synthesized by Pd-catalyzed coupling of 1-iodo-4-vinylbenzene with NaCH(CN)<sub>2</sub>. Subsequent Heck-coupling of **1** and **3** affords precursor **4**, which is then alkylated and

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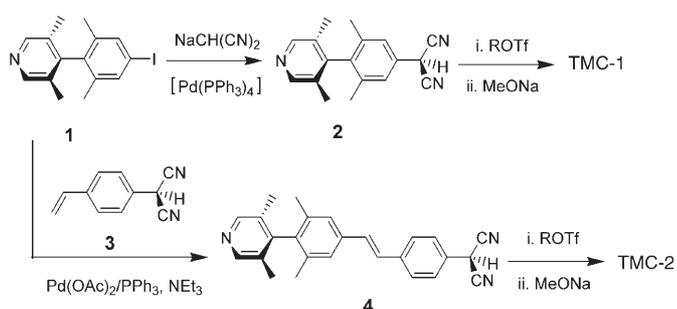
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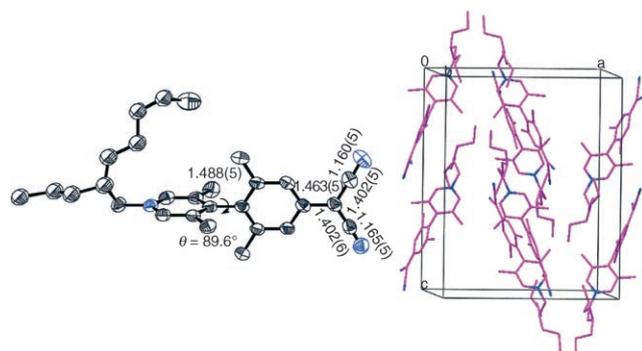
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**Scheme 2.** Synthesis of twisted  $\pi$ -electron chromophores. Tf = trifluoromethanesulfonyl.

deprotonated to yield TMC-2. The new zwitterions are air- and moisture-stable, purifiable by column chromatography, and were characterized by conventional techniques.<sup>[12]</sup> Thermogravimetric analysis indicates very high chromophore thermal stability ( $T_d \approx 306^\circ\text{C}$  for TMC-1,  $\approx 330^\circ\text{C}$  for TMC-2),<sup>[12]</sup> while  $^1\text{H}$  NMR indicates stability in  $[\text{D}_6]\text{DMSO}$  solution at  $150^\circ\text{C}$  for periods of hours under air.

Single-crystal diffraction data for TMC-1<sup>[13]</sup> reveal a large arene–arene dihedral twist angle ( $89^\circ$ ; Figure 1). The fact that twisting is governed primarily by tetra-*ortho*-methylbiaryl

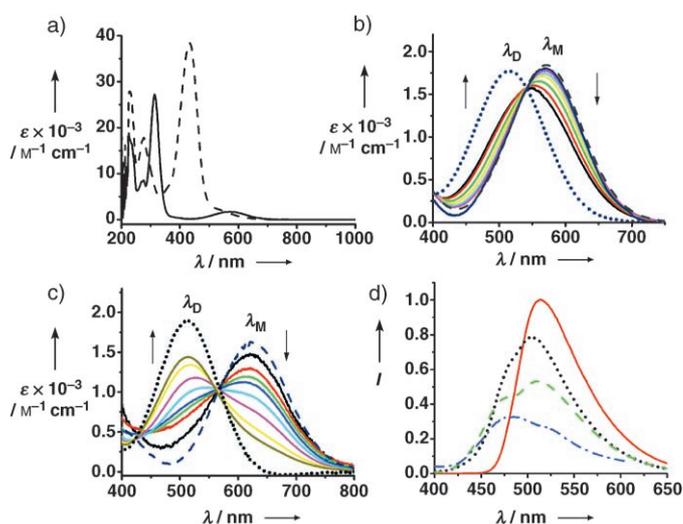


**Figure 1.** Left: ORTEP drawing (50% probability ellipsoids) of the TMC-1 molecule. Hydrogen atoms are omitted for clarity. Right: Packing diagram.

steric interactions and is independent of chromophore architecture is argued by nearly identical angles in several other TMC-type molecules.<sup>[10]</sup> The TMC-1 (ring)C–C(ring) distance ( $1.488(5) \text{ \AA}$ ) is close to that in typical biphenyls ( $\approx 1.487 \text{ \AA}$ ),<sup>[14]</sup> indicating steric crowding, consequent reduction in inter-ring  $\pi$ -conjugation, and departure from quinoidal structures where (ring)C=C(ring)  $\approx 1.349 \text{ \AA}$ .<sup>[14]</sup> The phenylenedicyanomethanide fragment displays different bond length patterns than in typical TCNQs;<sup>[14,15]</sup> the (NC)<sub>2</sub>C-bound phenylene ring has less quinoidal character, and the (dicyanomethanide)C–C(aryl) distance ( $1.463(5) \text{ \AA}$ ) lacks TCNQ C=C(CN)<sub>2</sub> exocyclic character ( $\approx 1.392 \text{ \AA}$ ).<sup>[14]</sup> This metrical pattern indicates negative charge localization on the C(CN)<sub>2</sub> group, also evident from C–CN bond shortening and C≡N bond elongation (TCNQ distances are  $1.427 \text{ \AA}$  and  $1.144 \text{ \AA}$ , respectively).<sup>[14]</sup> Finally, there is significant pyridinium aromatic character, with molecular dimensions paralleling those in *N*-methyl-*p*-phenylpyridinium salts<sup>[16]</sup> rather

than in cyclopentadienylidene-1,4-dihydropyridines.<sup>[17]</sup> Together, these metrical parameters confirm a charge-separated zwitterionic TICTOID ground state. Importantly, close correspondence between solid-state  $^{13}\text{C}$  NMR and optical spectra and those recorded in solution<sup>[12]</sup> argue that this structure persists essentially unchanged in solution.<sup>[18]</sup> As might be expected, the present zwitterion packs centrosymmetrically in pairs (Figure 1), likely a result of electrostatic dipole–dipole interactions (reasonable considering the large computed dipole moments).<sup>[19]</sup>

Optical spectra further support a zwitterionic ground state, with oscillator strengths unexceptional for two-level chromophores.<sup>[1–5]</sup> Thus, TMC-1 exhibits two fairly short wavelength maxima, assigned to pyridinium and phenyl subfragment high-energy intra-ring excitations, and one low-energy inter-subfragment charge-transfer (CT) excitation (Figure 2 a).<sup>[8]</sup> The TMC-1 CT bands exhibit strong negative



**Figure 2.** a) Optical absorption spectra of TMC chromophores in  $\text{CH}_2\text{Cl}_2$  solution. Solid line: TMC-1; dashed line: TMC-2. b, c) Concentration-dependent TMC-1 spectra in  $\text{CH}_2\text{Cl}_2$  solution (b) ( $3.0 \times 10^{-3}$ – $2.0 \times 10^{-5} \text{ M}$ ) and in  $\text{CHCl}_3$  solution (c) ( $5.6 \times 10^{-4}$ – $4.5 \times 10^{-6} \text{ M}$ ). Arrows indicate changes in CT bands upon dilution. The monomer (dashed line) and dimer (dotted line) spectra were derived from the data at two different concentrations and  $K_{\text{dimerize}}$ . d) Variable-concentration fluorescence spectra ( $\lambda_{\text{ex}} = 300$ – $350 \text{ nm}$ ) of TMC-2 in  $\text{CH}_2\text{Cl}_2$ . Intensities are normalized.  $I$  = fluorescence intensity. Solid line:  $5 \times 10^{-4} \text{ M}$ , dotted line:  $5 \times 10^{-5} \text{ M}$ , dashed line:  $5 \times 10^{-6} \text{ M}$ , dash-dotted line:  $2.5 \times 10^{-6} \text{ M}$ .

solvatochromism – large blue-shifts with increasing the solvent polarity (Table 1), indicating that the ground state dipole moment is substantially larger than in the excited state, consistent with the dominant zwitterionic ground state (and a negative  $\beta$ ). TMC aggregation observed in the solid state is further evidenced in  $\text{CH}_2\text{Cl}_2$  solution by concentration-dependent optical spectra (Figure 2 b), exhibiting a red-shift and increase of CT band intensity upon dilution in the range of  $10^{-3}$ – $10^{-4} \text{ M}$  (H-aggregation), with an isosbestic point supporting well-defined aggregation equilibria.<sup>[20]</sup>

To estimate binding energetics, the TMC-1 extinction coefficient was analyzed<sup>[20]</sup> as a function of concentration,

**Table 1:** Solvatochromic optical spectroscopic data and estimated changes in dipole moment from ground to excited state for TMC chromophores in selected solvents.<sup>[a]</sup>

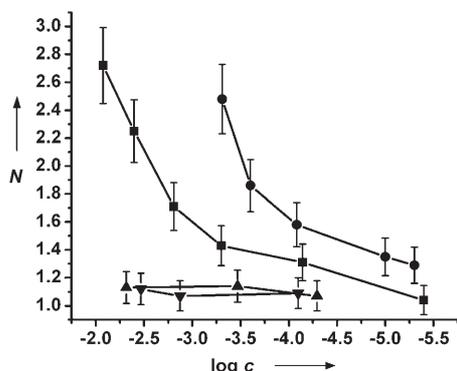
Solvent ( $E_T$ )	TMC-1			TMC-2		
	$\lambda_{\max}$ ( $\epsilon$ ) <sup>[b]</sup>	$\lambda_{\max}$ ( $\epsilon$ ) <sup>[c]</sup>	$\Delta\mu$ <sup>[d]</sup>	$\lambda_{\max}$ ( $\epsilon$ ) <sup>[b]</sup>	$\lambda_{\max}$ ( $\epsilon$ ) <sup>[c]</sup>	$\Delta\mu$ <sup>[d]</sup>
MeOH (0.76)	297	451	64	397	–	151
DMF (0.40)	310	478		427	–	
CH <sub>2</sub> Cl <sub>2</sub> (0.31)	314 (27 200)	569 (1840)		433 (38 400)	540 <sup>[e]</sup> (2090)	
THF (0.21)	320	592		451	578 <sup>[e]</sup>	

[a]  $\lambda_{\max}$  in nm,  $\epsilon$  in  $\text{M}^{-1}\text{cm}^{-1}$ ,  $\Delta\mu$  in  $10^{-30}$  C m. Solvent polarity given by the normalized  $E_T$  parameter. [b] Assigned to intra-subfragment excitation. Another high-energy subfragment excitation overlaps with the solvent (except CH<sub>2</sub>Cl<sub>2</sub>) and is not tabulated here. [c] Assigned to low-energy inter-subfragment charge-transfer (CT) excitation. [d] DFT-derived change in dipole moment from ground to excited state. [e] Deconvoluted from the subfragment excitation band and assigned to inter-subfragment CT.

assuming a simple dimerization model, and yields  $K_{\text{dimerize}} = 250 \pm 30 \text{ M}^{-1}$  and  $\Delta G_{\text{dimerize}}^\circ = -13.6 \pm 0.3 \text{ kJ mol}^{-1}$  in CH<sub>2</sub>Cl<sub>2</sub>. Concentration-dependent TMC-1 studies (Figure 2c) in less polar CHCl<sub>3</sub> yield larger  $K_{\text{dimerize}}$  and  $\Delta G_{\text{dimerize}}^\circ$  values of  $13\,300 \pm 1420 \text{ M}^{-1}$  and  $-23.5 \pm 0.3 \text{ kJ mol}^{-1}$ , respectively, not unexpectedly indicating that the aggregation is weaker in more polar solvents and also somewhat stronger than in typical planar merocyanine zwitterions.<sup>[20]</sup>

The TMC-2 spectrum features an intense band at 433 nm in CH<sub>2</sub>Cl<sub>2</sub> doubtless involving stilbenyl subfragment excitation,<sup>[8b]</sup> overlapping a weaker CT band centered at 540 nm (Figure 2a). Both subfragment and CT bands again exhibit negative solvatochromism (Table 1). Variable-concentration TMC-2 fluorescence spectra (Figure 2d) reveal a clear transition from dimer (515 nm) to monomer (485 nm) in the range of  $5 \times 10^{-4}$ – $2.5 \times 10^{-6} \text{ M}$ , providing confirmation of aggregation.

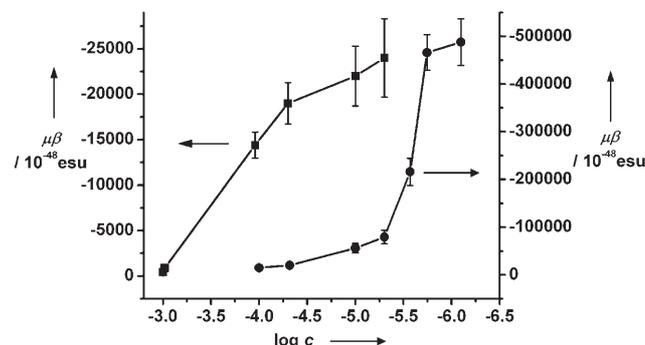
Additional quantitative information on the state of TMC chromophore aggregation is provided by PGSE (pulsed field gradient spin-echo) NMR spectroscopy (Figure 3).<sup>[21]</sup> Here, experimentally determined translational self-diffusion coefficients ( $D_t$ ), hydrodynamic radii ( $r_H$ ), volumes ( $V_H$ ), and the ratio between  $V_H$  and the van der Waals volume afford aggregation numbers ( $N$ ) readily identifying the aggregation level in solution ( $N = 1.0, 1.5$ , or  $2.0$  means 100% monomer, 50% monomer + 50% dimer, or 100% of dimer, respecti-



**Figure 3.** PGSE NMR-derived aggregation numbers ( $N$ ) as a function of concentration for chromophores TMC-1 in CD<sub>2</sub>Cl<sub>2</sub> (●) and [D<sub>6</sub>]DMSO (▲), and TMC-2 in CD<sub>2</sub>Cl<sub>2</sub> (■) and [D<sub>6</sub>]DMSO (▼). Lines are drawn as guides to the eye.  $c$  = concentration [M].

vely).<sup>[21c]</sup> The trends in  $N$  versus  $\log c$  (Figure 3) clearly show that monomer predominates in [D<sub>6</sub>]DMSO ( $\epsilon_r^{25} =$  relative permittivity at 25 °C = 46.45) for both TMC-1 and TMC-2 over the entire concentration range (see Supporting Information). In CD<sub>2</sub>Cl<sub>2</sub> ( $\epsilon_r^{25} = 8.93$ ), TMC-1 is exclusively monomeric only at the lowest concentrations examined ( $4 \times 10^{-6} \text{ M}$ , Supporting Information) while dimers (see Supporting Information) and even larger aggregates (Figure 3, Supporting Information) are present at the highest concentrations (Figure 3). TMC-2 exhibits a greater aggregation tendency and is not exclusively monomeric even at  $5 \times 10^{-6} \text{ M}$  (see Supporting Information). For TMC-2, aggregates larger than dimers are present at the highest concentrations (Figure 3, Supporting Information).

Hyperpolarizabilities were measured at 1907 nm in CH<sub>2</sub>Cl<sub>2</sub> by electric field-induced second harmonic generation (EFISH)<sup>[22]</sup> and track the same concentration-dependence as observed in the optical and PGSE spectra. Thus, the TCM-1 and TCM-2  $\mu\beta$  values show pronounced concentration dependence due to the aforementioned aggregation effects (Figure 4). The TCM-1  $\mu\beta$  rapidly increases as concentration falls, with  $\mu\beta$  saturating at a very large<sup>[1–5]</sup>  $-24\,000 \pm 4\,320 \times 10^{-48} \text{ esu}$  at  $5 \times 10^{-6} \text{ M}$ . The increase with dilution indicates



**Figure 4.** EFISH-derived  $\mu\beta$  data for chromophores TMC-1 (■) and TMC-2 (●) versus concentration in CH<sub>2</sub>Cl<sub>2</sub> at 1907 nm. Lines are drawn as guides to the eye.  $c$  = concentration [M].

dissociation of (presumably centrosymmetric) aggregates, paralleling the PGSE data, as expected. Note that  $\mu\beta$  approaches a maximum at concentrations where the PGSE measurements indicate the presence of more than 80% monomer. TCM-2 deaggregation occurs at somewhat lower concentrations ( $10^{-5}$ – $10^{-6} \text{ M}$ ), in good agreement with the PGSE data, with an unprecedented  $\mu\beta$  value of  $-488\,000 \pm 48\,800 \times 10^{-48} \text{ esu}$  at  $8 \times 10^{-7} \text{ M}$ .<sup>[23]</sup> From the reliably computed  $\mu$ <sup>[19]</sup> we estimate  $\beta_{0.65\text{eV}} \approx 9800 \times 10^{-30} \text{ esu}$ . To our knowledge, these are the largest off-resonance  $\mu\beta$  and  $\beta$  values ever achieved for any molecule.<sup>[1–5]</sup>

Preliminary Teng and Man<sup>[24]</sup> measurements on poled TMC-1 and TMC-2 containing guest–host polymers reveal very large EO coefficients ( $r_{33}$ ) at 1310 nm. Poly(vinylphenol) films containing 10 wt % TMC-1 and 5 wt % TMC-2, poled at  $100 \text{ V } \mu\text{m}^{-1}$ , exhibit nonresonant  $r_{33}$  responses of 48 and  $320 \text{ pm V}^{-1}$ , respectively. Lower EO responses are observed in less polar matrices, presumably due to the aggregation. These results suggest obvious molecular and macromolecular modification strategies, currently under investigation, to address the aggregation issue and to further enhance  $r_{33}$ .

In summary, twisted  $\pi$ -electron system chromophores have been prepared and exhibit exceptional molecular hyperpolarizabilities, with nonresonant  $\mu\beta$  values as high as  $-488000 \times 10^{-48}$  esu, while preliminary poled guest–host experiments indicate promise for EO applications. An interesting observation here is that the ultralarge hyperpolarizabilities exhibited by these unconventional chromophores seem far beyond classical two-level behavior. Kuzyk argues that the  $\beta$  responses of all organic chromophores prepared to date fall far short of the theoretical quantum limits, for reasons that are presently not entirely clear.<sup>[25]</sup> Twisted  $\pi$ -electron system chromophores may provide new insight into the reasons.

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