CHEMISTRY OF MATERIALS

Bistability of Fc-PTM-Based Dyads: The Role of the Donor Strength

Judith Guasch,[†] Luca Grisanti,^{‡,⊥} Stefan Jung,[§] Dayana Morales,[†] Gabriele D'Avino,^{‡,#} Manuel Souto,[†] Xavier Fontrodona,^{||} Anna Painelli,^{‡,*} Franz Renz,[§] Imma Ratera,[†] and Jaume Veciana^{†,*}

[†]Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)/CIBER-BBN, Campus de Bellaterra, E-08193 Cerdanyola del Vallès, Spain

[‡]Dipartimento Chimica, GIAF, Parma University/INSTM-UdR, I-4310, Parma, Italy

[§]Institute of Inorganic Chemistry, Leibniz University Hannover, Callinstr. 9, D-30167 Hannover, Germany

^{II}Serveis Científico-Tècnics, Campus de Montilivi, University of Girona, E-17071 Girona, Spain

Supporting Information



ABSTRACT: Bistability of valence tautomeric donor—acceptor dyads formed by covalently linking a ferrocene-based electrondonor and the perchlorotriphenylmethyl radical, as the electron-acceptor, is tuned via a chemical modification of the ferrocene group. Specifically, the methylation of the ferrocene unit increases the strength of the donor group stabilizing the zwitterionic state in polar solvents and leading to an intriguing coexistence of neutral and zwitterionic species in solvents of intermediate polarity. Bistability in the crystalline phase is demonstrated by temperature dependent Mössbauer spectra. This complex and interesting behavior is quantitatively rationalized in the framework of a bottom-up modeling strategy. Optical spectra in solution are first analyzed to extract and parametrize an effective two-state molecular model, which is then adopted to rationalize the observed bistability in the solid state as due to cooperative electrostatic interchromophore interactions.

KEYWORDS:

Bistability, valence tautomers, intramolecular electron-transfer, optical spectroscopy, solvatochromism, Mössbauer spectroscopy.

INTRODUCTION

Bistability, the property of a material to be found in two different stable states in the same external conditions,¹ represents the extreme manifestation of the nonlinear response of the material to an external stimulus and is only supported in systems with strong cooperative interactions. Bistability is therefore a rare phenomenon in molecular materials.² However, the possibility to switch a bistable molecular material between states having strikingly different properties by the application of (possibly tiny) external stimuli (like, e.g., small variations of temperature or pressure, applied electric or magnetic field, or even illumination) opens the way to the development of molecular-based switches and memories:³⁻¹⁴ bistable molecular materials are in demand to build very fundamental molecular electronic devices.

Valence-tautomeric molecules are obvious building blocks for bistable molecular materials. A few years ago, a new and promising valence tautomeric compound, Fc-PTM, was synthesized by Veciana and co-workers.¹⁵ In this system, a ferrocene (Fc) moiety, acting as electron-donor (D), is linked through a conjugated vinylene bridge to the perchlorotriphenylmethyl (PTM) radical, a strong electron-acceptor (A).^{15–18} Absorption spectra of Fc-PTM solutions¹⁸ show a band in the near-infrared region related to the intramolecular electron transfer (IET) between the ferrocene donor (D) and the PTM acceptor (A). The band shows a strong positive solvatochromism, shifting from 892 nm in *n*-hexane to 1003 nm in DMSO, unambiguously pointing to a neutral (DA) ground state of Fc-PTM in solution. Accordingly, an intense absorption at 387 nm,^{17–20} assigned to the neutral PTM radical, is observed in all solvents, while the absorption feature at 490 nm, ascribed to the PTM anion,^{17,18,21,22} is not present. The IET absorption of Fc-

Received:January 14, 2013Revised:February 10, 2013Published:February 12, 2013

Chemistry of Materials

PTM locates the zwitterionic (D^+A^-) state, reached upon photoexcitation in solution, at an energy more than 1.3 eV higher than the neutral ground state,^{18,23} a fairly high energy that sharply contrasts with the observed coexistence in a wide temperature range of the neutral and the zwitterionic forms of Fc-PTM in the crystalline phase, as demonstrated by temperature dependent Mössbauer spectra.¹⁷

This complex phenomenology was understood in a comparatively simple and coherent picture based on a bottom-up modeling strategy.²³ Specifically, solution spectra of Fc-PTM were analyzed based on a two-state model explicitly accounting for the coupling between electronic and vibrational degrees of freedom as well as for polar solvation. The resulting molecular model was then used to describe interacting molecules in the crystalline phase. Within this picture, the coexistence of the neutral and zwitterionic phases in the solidstate is quantitatively ascribed to bistability induced in the system by cooperative electrostatic intermolecular interactions. Fc-PTM then offered the first, and so far unique, experimental realization of bistability in crystals of neutral DA molecules, as theoretically predicted ten years ago.^{24,25} Few other bistable molecular systems based on ferrocenyl-conjugated pyrylium salts have been described. In these systems, electrostatic interactions also involve couterions that play a major role, in contrast to the neutral Fc-PTM.²⁶

Herein, we report the synthesis of a new valence tautomeric compound, Me_8Fc -PTM (Figure 1), with the same skeleton as



Figure 1. Molecular structures relevant to the neutral DA (purple, \bullet) and zwitterionic D⁺A⁻ (yellow, \bullet) states of Me₈Fc-PTM.

Fc-PTM, but with eight methyl groups attached to the ferrocene subunit in order to increase its donor strength. An extensive characterization of Me_8Fc -PTM in solution and in the crystalline phase is presented, demonstrating that, at variance with Fc-PTM, Me_8Fc -PTM in solution can be found in the neutral (DA) and/or zwitterionic (D⁺A⁻) forms, depending on the solvent polarity, while, much as with Fc-PTM, true bistability is observed in the solid state.

EXPERIMENTAL SECTION

Synthesis. Me₈Fc-PTM (Figure 1) was synthesized in three steps with a good yield (83%) (Scheme 1).

The protonated phosphonate PTM derivative 1^{27} and the 1-formyl-2,2',3,3',4,4'5,5'-octamethylferrocene $2^{28,29}$ yielded compound 3 through a Horner-Wadsworth-Emmons reaction. The deprotonation of compound 3 with potassium hydroxide gave 4, which was stabilized using 18-Crown-6. The oxidation of 4 with silver nitrate afforded Me₈Fc-PTM, which is very stable under atmospheric conditions in solid state. Dark-brown crystals of Me₈Fc-PTM were obtained by a slow-evaporation from a solution of CH₂Cl₂:hexane (2:3).

UV/vis/NIR Spectra. Optical absorption spectra of Me₈Fc-PTM, in Figure 2, show a pronounced solvent dependence in the whole spectral range. In low polarity solvents, from *n*-hexane to anisole, an intense and sharp absorption appears at 25 840 cm⁻¹ (387 nm), corresponding to a well-characterized transition of the neutral PTM radical.^{17–20} In the strongly polar solvent dimethylformamide (DMF), the sharp band ascribed to the neutral PTM radical at 25 840 cm⁻¹ disappears,

Scheme 1. Synthesis of Me₈Fc-PTM



Figure 2. Absorption spectra of Me₈Fc-PTM in different solvents.

indicating that Me₈Fc-PTM is only present in the zwitterionic form (D⁺A⁻). Concomitantly, a very intense band shows up at 18 870 cm⁻¹ (530 nm), as expected for a PTM subunit in its anionic form.^{17,18,21,22} We conclude that the strong electron-donor character of the methylated ferrocene unit lowers the energy of the zwitterionic state of Me₈Fc-PTM, so that, at variance with Fc-PTM that stays in the neutral (DA) form in all solvents,^{23,30} the ground state of Me₈Fc-PTM changes from neutral in low-polarity solvents to zwitterionic in strongly polar solvents.

In acetone, an intermediate polarity solvent, the Me₈Fc-PTM spectrum shows both the band due to the neutral PTM radical at 25 840 cm⁻¹ and that due to the PTM anion at 18 870 cm⁻¹, pointing to the coexistence of the neutral and zwitterionic species in this solvent. Therefore, it is possible to tune the solvent polarity as to drive the equilibrium between the neutral and the zwitterionic states of Me₈Fc-PTM, eventually forcing the system into a coexistence regime.

The weak band observed around 15 400 cm⁻¹ (650 nm) is assigned to a π -bridge-to-PTM electron transfers, as found for other π conjugated PTM radicals.^{18,23,30} Finally, the lowest energy band, located around 7500 cm⁻¹ (1300 nm) in low-polarity solvents, is ascribed to the IET resonance between the neutral and the zwitterionic forms of Me₈Fc-PTM, and its solvent dependence will be analyzed based on the theoretical model discussed in the next section.

Mössbauer Spectra. The Mössbauer spectrum recorded at 295 K on Me₈Fc-PTM crystalline powders is reported in Figure 3a and relevant data are summarized in Table 1. It shows two doublets: the first doublet, with an isomer shift IS = 0.418 mm/s relative to α -iron and a quadrupole splitting Δ = 2.326 mm/s, is assigned to the Fe (II) ion in the ferrocene unit.¹⁷ The second doublet, with a smaller Δ = 0.594 mm/s, is attributed to Fe (III) ion, in the ferrocenium cation.¹⁷ The relative area of the two signals amounts to 32% and 68%, respectively, suggesting that at room temperature the neutral (DA) and zwitterionic (D⁺A⁻) forms of Me₈Fc-PTM coexist in the crystals, with a predominance of the zwitterionic form. The spectrum collected



Figure 3. (a) Mössbauer spectrum of a crystalline sample of Me_8Fc -PTM at 295 K; (b) the same as (a) at 85 K; (c) Mössbauer spectrum of a crystalline sample of compound 3 at 295 K; (d) the same as (c) at 78 K. Blue curves in (a), (b), and (c) are fitted spectra calculated summing the contributions from Fe(III) (red curves) and Fe(II) (green curves), according to the data in Table 1 (for (c) the Fe(III) contribution vanishes). In (d) the total fit is obtained summing over two Fe(II) contributions (green curves).

Table 1. Parameters of the Mössbauer Spectra of Crystalline Samples of Me₈Fc-PTM and Its Protonated Precursor 3 at Room and Low Temperatures

compound	Т (К)	assignment	$IS (mm/s)^a$	$\Delta (\text{mm/s})^b$	site population (%)		
Me ₈ Fc- PTM	295	Fe (II)	0.418(35)	2.325(71)	32		
		Fe (III)	0.127(37)	0.593(68)	68		
	85	Fe (II)	0.517(43)	2.281(86)	88		
		Fe (III)	0.162(35)	0.493(60)	12		
3	295	Fe (II)	0.286(21)	2.396(43)	100		
		Fe (II)	0.416(72)	2.252(24)	73		
	78	Fe (II)	0.412(14)	2.957(41)	27		
^{<i>a</i>} Isomer shift. ^{<i>b</i>} Quadrupole splitting.							

at 85 K (Figure 3b) shows the same features, but with a predominance of the neutral species, amounting to 88% of the total.

Panels c and d of Figure 3 show Mössbauer spectra of 3, the protonated precursor of Me_8Fc -PTM, at 295 and 78 K, respectively. In this compound the iron ion has exactly the same environment as in Me_8Fc -PTM, but IET is prevented due to the protonation of the PTM unit. Only the Fe (II) doublet is observed in Mössbauer spectra of 3 at all temperatures (Figure 3c,d), with no hint of Fe (III). The complex

structure observed at 78 K is safely assigned to the presence of slightly different structures of compound **3**. On this basis, we rule out the possibility that the doublet ascribed to the Fe (III) ion in Mössbauer spectra of Me₈Fc-PTM is due to thermal motion of the iron ion inside the ferrocene moiety, and confirm the coexistence of the neutral and zwitterionic forms in the crystal.

X-ray Diffraction Analysis. Single crystal X-ray diffraction data were collected from small dark-brown crystals of Me_8Fc -PTM at 300 and 100 K (details are reported in the Supporting Information, SI). The ferrocene and PTM subunits do not show any significant structural change upon lowering temperature (SI Table S2 and S3). Indeed, it is known that the geometry of the PTM group is marginally affected when going from the radical to the anionic form.³¹ Moreover, the detailed study of Fc-based materials in ref 26, similarly suggests marginal structural variation of the Fc group with its charge. The only relevant structural variation with temperature is seen in the vinylene-bridge region, where the difference between the single (C–C) and double (C=C) bond lengths amounts to 0.250 Å at 300 K and decreases to 0.095 Å at 100 K, suggesting a weaker conjugation in the zwitterionic than in the neutral forms of Me_8Fc -PTM.

RESULTS AND DISCUSSION

Molecular Model and Solvatochromism. The two-state model for open and closed shell donor–acceptor dyads has been presented in previous publications^{23,30,32–34} and is shortly summarized here. The low-energy electronic structure of the dyads, governed by the charge resonance between the neutral (DA) and the zwitterionic (D⁺A⁻) states, is captured in its essence by the two-state Mulliken Hamiltonian:

$$h_{\rm el}(z, \tau) = 2z |D^{+}A^{-}\rangle \langle D^{+}A^{-}| - \tau (|DA\rangle \langle D^{+}A^{-}| + |D^{+}A^{-}\rangle \langle DA|)$$
(1)

where 2z is the energy required to turn a neutral DA pair into the zwitterionic state and τ is the hybridization energy mixing the two states. The diagonalization of the above Hamiltonian leads to a mixed-valence ground state, $D^{+\rho}A^{-\rho}$, characterized by a molecular ionicity, ρ , ranging from 0 (fully neutral dyad) to 1 (fully zwitterionic dyad).

This minimal model is empirical and must be validated against the evolution of absorption spectra with solvent polarity. To such an aim, the model must be extended to account for the coupling between electrons and molecular vibrations and for the effects of polar solvation. The adiabatic Hamiltonian, including the linear coupling to a vibrational coordinate, q, and to an effective solvation coordinate proportional to the orientational component of the solvent reaction field, $F_{\rm or}$, reads:^{23,30,32–34}

$$h_{\rm sol}(z_{\rm sol},\,\tau) = h_{\rm el}(z_{\rm sol},\,\tau) + \frac{1}{2}\omega_{\nu}q^2 + \frac{\mu_0}{4\varepsilon_{\rm or}}F_{\rm or}^2$$
(2)

where $2z_{\rm sol} = 2z - \omega_{\nu}(2\varepsilon_{\nu})^{1/2}q - \mu_0F_{\rm or}$ is the *q*- and $F_{\rm or}$ -dependent ionization energy of the DA dyad, ω_{ν} is the frequency of the vibrational mode, ε_{ν} is the vibrational relaxation energy, μ_0 is the dipole moment of the D⁺A⁻ state (following Mulliken all other matrix elements of the dipole moment operator are neglected), and $\varepsilon_{\rm or}$ is the orientational component of the solvent relaxation energy.

The solvent reaction field F_{or} is treated as a classical coordinate, hence calculated absorption spectra are the Boltzmann-weighted average of spectra obtained for different values of $F_{or}^{23,34,35}$ It is worth reminding that molecular parameters, as extracted from the analysis of solution absorption spectra, implicitly account for the effect of fast electronic polarization of a generic organic nonpolar medium,

and can therefore be employed to model mutually interacting molecules in bichromophoric species, $^{37-40}$ in films 33,41 as well as in the solid state. 23,33

Figure 4 compares experimental and calculated absorption spectra of Me₈Fc-PTM in the IET region. Calculated spectra



Figure 4. Experimental (a) and calculated (b) IET band of Me₈Fc-PTM in different solvents. Calculated spectra were obtained with molecular parameters in Table 1 and $\varepsilon_{\rm or}$ values listed in the panel b.

Table 2. Molecular Parameters of Me₈Fc-PTM (eV)

z	τ	\mathcal{E}_{v}	$\omega_{ m v}$
0.42	0.30	0.12	0.18

are based on molecular parameters listed in Table 2 and on $\varepsilon_{\rm or}$ values shown in Figure 4b. In low polarity solvents (*n*-hexane, CHCl₃, CH₂Cl₂, and anisole) Me₈Fc-PTM is in a largely neutral ground state, with calculated ρ values slightly increasing from 0.097, in *n*-hexane, to 0.120, in anisole. As expected for a largely neutral chromophore,^{34,36} a progressive red shift of the IET band is calculated with increasing solvent polarity, in excellent agreement with experimental spectra.

In DMF, the most polar solvent considered here, Me_8Fc_PTM is zwitterionic, as inferred from the absence of the sharp absorption of neutral PTM radical at 25840 cm⁻¹ (see Figure 2). Concomitantly, the IET absorption band ascribed to the neutral DA specie disappears. Our model describes a largely ionic ground state ($\rho = 0.972$) in strongly polar solvents ($\varepsilon_{or} = 1.2 \text{ eV}$). In these conditions, a weak and broad IET absorption is calculated around 14 500 cm⁻¹ (cf Figure 4b), at higher frequency than in less polar solvents. This feature is consistent with the weak and broad band observed around 14 000 cm⁻¹ in spectra collected in DMF solutions (Figure 4a).

The evolution from a neutral to a zwitterionic ground state with increasing solvent polarity and the coexistence of the two states in intermediate polarity solvents is well captured by the model. Specifically, in Figure 5, the black lines in each panel show the ground state energy as a function of the solvent reaction field, F_{or} , calculated for Me₈Fc-PTM with the model parameters in Table 2 and four different values of ε_{or} as to mimic increasing solvent polarity. In low polarity solvents (panels a and b in Figure 5, corresponding to CHCl₃ and CH₂Cl₂, respectively) the energy of the neutral basis state (violet line) is much lower than the energy of the zwitterionic basis state (orange line), so that the ground state potential energy surface (black line) is similar to the potential energy



Figure 5. Black continuous curves: ground state energy calculated for Me_8FcPTM as a function of the reaction field, F_{or} for (a) $\varepsilon_{or} = 0.18$ eV (corresponding to CHCl₃), (b) 0.35 eV (CH₂Cl₂), (c) 0.8 eV (acetone), and (d) 1.2 eV (DMF). Violet and orange lines show the energies of DA and D⁺A⁻ state, respectively. Black dashed line shows the room temperature Boltzmann probability distribution calculated based on the ground state energy.

surface of the neutral (DA) state (violet line). In low-polarity solvents then, the system is in a largely neutral state.

In strongly polar solvents (Figure 5d) the zwitterionic state is greatly stabilized by the interaction with the polar solvent and the ground state potential energy surface (black line) shows a deep minimum corresponding to the zwitterionic state (the energy of the D^+A^- state is shown as the orange line). At room temperature, only the zwitterionic state is populated (black dashed line showing the relevant distribution). In the intermediate regime (Figure 5c), the potential energy surfaces corresponding to the two neutral and zwitterionic states (violet and orange lines, respectively) have similar energies and, since the mixing matrix element is not too large, the ground state potential energy surface (black line) shows two minima corresponding to largely neutral and zwitterionic states. As shown by the Boltzmann distribution (black dashed line), both states are populated at ambient temperature, in agreement with experimental results for acetone solutions.

Before closing this section, we shortly compare the spectroscopic behavior of Me_8Fc -PTM and its nonmethylated and fully methylated analogues, Fc-PTM and Me_9Fc -PTM, respectively. As discussed before, the nonmethylated Fc group is too poor a donor to stabilize the zwitterionic state in solution: Fc-PTM stays neutral in all solvents.^{23,30} Increasing the donor strength by methylation favors the zwitterionic state and the fully methylated Me_9Fc -PTM analogue behaves in a similar way as Me_8Fc -PTM, switching to a zwitterionic state in strongly polar solvents, as demonstrated by solution spectra in SI Figure S4.

This behavior is rationalized in our model by a smooth decrease of 2*z*, the energy difference between the neutral and zwitterionic basis states, with increasing the number of methyl substituents. Specifically, *z* ranges from 0.61 eV for Fc-PTM²³ to 0.42 eV for Me₈Fc-PTM, and 0.36 eV for Me₉Fc-PTM,³⁰ in line with the increasing donating character of the ferrocene unit with successive methylation. The other model parameters (cf Table 2) are exactly the same for the two methylated

compounds, in line with the strong similarity between the two compounds.

Modeling Bistability in the Solid State. To describe the bistability of Me_8FcPTM in the solid state we adopt the same bottom-up modeling strategy that was successfully applied to the nonmethylated system, Fc-PTM.^{2,23,30} Specifically, the molecular model parameters in Table 2, extracted from the analysis of solution spectra of Me_8FcPTM , are implemented in a model for Me_8FcPTM crystals, where electrostatic intermolecular interactions are introduced in the mean-field approximation. The mean-field Hamiltonian for a crystal of DA molecules reads:^{2,23,25,30}

$$H_{\rm cry}(z_{\rm cry}, \tau) = h_{\rm el}(z_{\rm cry}, \tau) + \frac{1}{2}\omega_{\rm v}q^2 - M\rho^2$$
(3)

where $h_{\rm el}(z_{\rm cry}, \tau)$ is the two state electronic Hamiltonian defined in eq 1, but accounting for the crystalline value of the molecular parameter z. Specifically, $2z_{\rm cry}$ is the effective energy required to switch a single molecule from the neutral (DA) to the zwitterionic (D⁺A⁻) state when the molecule is embedded into a crystal of molecules in the relevant ground state. This energy then self-consistently depends on the degree of charge transfer of the molecules in the crystal, $\rho: z_{\rm cry}(\rho) = 2z - 2\varepsilon_v\rho + 2M\rho$. In these equations, the information about the crystal is fully conveyed by *M*, the electrostatic (Madelung) energy of a lattice of molecules in the zwitterionic D⁺A⁻ state.^{2,23,25,30} For attractive intermolecular interactions, *M* is negative and the energy required to create a zwitterionic molecule is reduced in the crystal.

The Hamiltonian in eq 3 is diagonalized for different values of $z_{\rm cry}$ to extract in a self-consistent approach the dependence of the molecular ionicity ρ on $M^{2,23,30}$. Figure 6a shows the



Figure 6. (a) Molecular ionicity as a function of *M* calculated based on the Hamiltonian in eq 3 and for molecular parameters in Table 2. Continuous and dashed lines refer to stable and unstable solutions, respectively; (b) black points (left scale) show the component of the dipole moment along the DA direction calculated for Me₈FcPTM as a function of the applied electric field; red squares (right scale) show the Madelung energy calculated according to eq 4. Closed and open symbols refer to results relevant to the room temperature and lowtemperature structure, respectively. Dipole moment and Madelung energy are calculated with the Coulson net atomic charges obtained at different values of *F*. The green dashed lines delimitate the region where the molecule is in a largely polar state ($\rho \approx 1$).

resulting $\rho(M)$ curve, calculated adopting molecular parameters in Table 2. The curve describes a crystal of largely neutral molecules ($\rho < 0.14$) for relatively weak electrostatic interactions (|M| < 0.67) and a crystal of zwitterions ($\rho >$ 0.93) for strong interactions (|M| > 0.87). In the intermediate region, the Hamiltonian in eq 3 has two stable solutions (continuous line), corresponding to a crystal of largely neutral or largely ionic molecules. Our model for the Me₈FcPTM crystal then supports bistability, provided the strength of electrostatic interactions, as measured by M, falls in the region -0.87 eV < M < 0.67 eV.

To confirm our model for bistability in Me₈FcPTM crystals we calculate M_1 according to the following expression:²³

$$M = \frac{1}{2} \sum_{m \neq n} \sum_{i,j} \frac{q_i q_j}{|r_i^m - r_j^n|}$$
(4)

where m and n count on the molecules in the crystal, i, j run on the atoms within each molecule, r_i^m denotes the position of atom *i* in molecule m_i and q_i is the charge on the *i*-th atom relevant to the molecule in the zwitterionic D⁺A⁻ state. To estimate these charges, we perform quantum chemical calculations using the PM6 Hamiltonian 42 (MOPAC 2007 package)⁴³ on an isolated (gas phase) Me₈FcPTM subject to an external electric field aligned along the DA axis (connecting the central C atom of PTM to the Fe atom).²³ Increasing the applied field drives the molecule from a largely neutral ground state (no field) to a zwitterionic state (large applied field). This is confirmed by data in Figure 6b (black, scale on the left side) that shows the component of the calculated dipole moment parallel to the applied field, $\mu_z = \sum_i z_i q_i$, as a function of the field. Closed and open symbols refer to results obtained for the molecular geometry extracted from the analysis of X-ray data at room and low temperature, respectively, and show similar behavior. Specifically, at low fields a smooth and almost linear $\mu_{z}(F)$ dependence is observed, safely ascribed to the molecule in a largely neutral ($\rho \approx 0$) state. With increasing field an abrupt jump in the calculated dipole is observed at $F \approx 0.3$ V/ Å, toward another region of smooth and almost linear behavior corresponding to larger values of the molecular dipole moment. This second region ($F = 0.4 \div 0.80$ V) is therefore ascribed to a largely zwitterionic ($\rho \approx 1$) state. Quite interestingly, the threshold field ~0.3 V/Å estimated for Me8FcPTM is lower than the value 0.45 V/Å previously obtained for the nonmethylated analogue, Fc-PTM,²³ in line with the stronger donor character of the methylated ferrocene group.

We are now in the position to estimate M, the Madelung energy of a crystal of zwitterionic molecules, as entering the self-consistent Hamiltonian in eq 3. The red squares in the right panel of Figure 6 show the Madelung energy calculated inserting in eq 4 the atomic charges computed for different values of the applied electric field (sums were performed on crystal supercells large enough to obtain converged values within 0.01 eV). Once again, closed and open circles refer to results obtained at room and low temperature, respectively. In all cases, Madelung energies estimated in the neutral regime are negligible with respect to the values obtained in the F-range relevant to the zwitterionic regime. The values of the Madelung energy estimated in the F-region relevant to zwitterionic states (the region roughly comprised between the two vertical dashed lines in Figure 6b) then define our best estimate for M = -0.7 \div -1.15 eV, as extracted from the room temperature structure and $M = -0.61 \div -0.98$ eV from the low-temperature structure. While the reduced M values estimated at low temperature are in line with the increased volume of the unit cell (see SI Table S1) as well as with the reduced content of zwitterionic species (see Table 1), the large uncertainties in the estimated values make this difference irrelevant. What is more important is that in both cases, the estimated interval of M values largely overlaps with the bistability window, -0.87 eV <M < 0.65 eV, predicted for Me₈FcPTM (see Figure 6a).

We then conclude that the proposed model quantitatively supports the hypothesis of bistability induced by electrostatic interactions in crystals of Me₈FcPTM, leading to a picture fully consistent with results previously obtained for the parent Fc-PTM system. Both molecules fulfill the requirements for bistability as dictated by the phase diagram in ref 2, namely a strict balance between the molecular ionization energy and the electrostatic interaction strength ($z \approx -2M$), combined with a low hybridization energy $(z > \tau)$. Nevertheless, the similarity between the two dyads is only formal. In fact, the valence tautomerism of the two compounds is characterized by very different values of ionization energy (z = 0.61 eV for Fc-PTM against 0.42 eV for Me₈Fc-PTM) in virtue of the stronger donor character of the substituted ferrocene group. This difference shows itself in the qualitatively different behavior of the two molecules in solution, with Fc-PTM remaining neutral even in strongly polar solvents,^{23,30} while Me₈Fc-PTM turns zwitterionic in polar solvents, showing coexistence in intermediate polarity solvents. In the crystalline phase, the relatively high ionization energy of Fc-PTM is counterbalanced by strong electrostatic interactions (M was estimated in the -1.5 to -1 eV range), while in Me₈Fc-PTM the estimated M values are considerably lower (between -1.15 and -0.75 eV, most probably due to the spacing effect of the bulky methyl groups), leading also in this case to a perfect matching of the stringent conditions for bistability.

CONCLUSIONS

A new donor-acceptor dyad Me₈Fc-PTM is synthesized and carefully characterized in solution and in the solid state, to provide a sound basis for a theoretical description of the observed phenomena of coexistence and bistability. Me₈Fc-PTM has a very strong electron donating group (the octamethylated ferrocene unit) linked through a vinylenebridge to a strong electron-acceptor (the perclorotriphenylmethyl radical). The energetic proximity of the neutral (DA) and zwitterionic (D^+A^-) structures in this system is well demonstrated by the possibility to tune the molecular charge distribution from a largely neutral state, $D^{\rho+}A^{\rho-}$ with $\rho \approx 0$, in nonpolar or mildly polar solvents, to a largely zwitterionic state, $D^{\rho+}A^{\rho-}$ with $\rho \approx 1$, in strongly polar solvents. States with intermediate charge-transfer ($D^{\rho+}A^{\rho-}$, with $\rho \approx 0.5$) are not accessible to the system because of the poor conjugation between the D and A groups: as a result, in intermediate polarity solvents (acetone) coexistence of largely neutral and largely zwitterionic species is experimentally observed. This intriguing behavior is qualitatively different from what observed for the parent nonmethylated compound, Fc-PTM that, due to the poorer donating character of the nonmethylated ferrocene unit, stays in a neutral state even in the strongly polar DMSO solvent.^{23,30} These features are quite naturally understood based on an essential two-state model parametrized to reproduce the IET band observed in the NIR region of optical absorption spectra. Quite interestingly, coexistence of neutral and zwitterionic species in solution has been recently observed in similar PTM-based dyads.⁴⁴ In these systems, a vinylene bridge connects the PTM acceptor to tetrathiafulvalene (TTF), a strong electron-donor: apparently the vinylene-bridge offers a poor conjugation path toward the PTM group, as required to observe coexistence of neutral and zwitterionic species in systems with strong donors.

While suggestive, coexistence of neutral and zwitterionic species in solution is not a signature of genuine bistability: in fact a fast equilibrium between the two forms is unavoidable in solution. True bistable behavior implies long-lived (noninterconverting) states that can only be achieved via strong cooperative interactions.² Indeed, according to an original theoretical suggestion,^{24,25} we have recently proved that electrostatic intermolecular interactions are a strong enough source of cooperativity to induce bistability in Fc-PTM crystals,²³ even if, in this specific system coexistence is not observed in solution.

Bistability is a rare phenomenon that requires a weak conjugation between the D and A group (small τ in the twostate model), as well as a very precise balance between the energy required to transfer a charge from the D to the A site (2z in the two-state model) and the electrostatic interchromophore interaction, measured in the proposed model for the crystal in terms of the Madelung energy relevant to a crystal of fully zwitterionic chromophores, M. Here we demonstrate that this very delicate balance, achieved for the parent Fc-PTM compound,²³ is also met for the methylated analogue, Me₈Fc-PTM: the methyl groups not only lower the energy required for the electron transfer, but also, due to their bulky nature, reduce intermolecular interactions, as to maintain the stringent conditions for bistability. Unfortunately, we were not able to collect Mössbauer spectra of the fully methylated compound (Me₉Fc-PTM): this system shows in solution a similar behavior as the octamethylated compound (see Supporting Information), but, having a stronger donor group and hence a lower zvalue, is expected to show a narrower bistability region,² making the requirement for the M vs z balance even more stringent.

The PTM-vinylene-bridge moiety represents a very promising building-block for valence-tautomeric molecules: a careful choice of the strength of the donor species to be connected to the bridge can lead to molecules whose ground state can be switched from neutral to zwitterionic changing the polarity of the surrounding medium, with the two species coexisting in media of intermediate polarity. Even more interestingly, the same systems can be designed to provide true bistability in the solid state, provided a careful matching of on-site and intersite interactions is achieved.

ASSOCIATED CONTENT

S Supporting Information

Detailed synthesis and characterization of compounds 3, 4, and Me_8Fc -PTM. Cyclic voltammetry, single crystal structure, and UV/vis/NIR of Me_9Fc -PTM. Crystallographic information files (CIF) for Me_8Fc -PTM at 300 and 100 K. This material is available free of charge via the Internet at http://pubs.acs.org

AUTHOR INFORMATION

Corresponding Author

*E-mail: anna.painelli@unipr.it (A.P.); vecianaj@icmab.es (J.V.).

Present Addresses

¹Laboratory for Chemistry of Novel Materials, University of Mons, Place du Parc 20, BE-7000 Mons, Belgium.

[#]Dipartimento di Chimica Industriale "Toso Montanari" and INSTM, Università di Bologna, Viale del Risorgimento 4, IT-40136 Bologna, Italy.

Author Contributions

The manuscript was written through contributions of all authors.

Chemistry of Materials

Funding

This work was supported by the DGI grant (POMAs; CTQ2010–19501), the Networking Research Center on Bioengineering, Biomaterials, and Nanomedicine (CIBER-BBN), and the Generalitat de Catalunya (grant 2009SGR00516).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J.G. is grateful to the Consejo Superior de Investigaciones Científicas (CSIC) for a "JAE" fellowship.

ABBREVIATIONS

IET, intramolecular electron transfer; D, electron-donor; A, electron-acceptor; PTM, perchlorotriphenylmethyl radical; Fc, ferrocene; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide

REFERENCES

- (1) Buchanan, R. M.; Pierpont, C. G. J. Am. Chem. Soc. 1980, 102, 4951.
- (2) D'Avino, G.; Grisanti, L.; Painelli, A.; Guasch, J.; Ratera, I.; Veciana, J. *CrystEngComm* **2009**, *11*, 2040.

(3) Roux, C.; Adams, D. M.; Itié, J. P.; Polian, A.; Hendrickson, D. N.; Verdaguer, M. Inorg. Chem. 1996, 35, 2846.

(4) Hauser, A.; Jeftic, J.; Romstedt, H.; Hinek, R.; Spiering, H. Coord. Chem. Rev. **1999**, 190–192, 471.

- (5) Ghosh, A.; Wondimagegn, T.; Gonzalez, E.; Halvorsen, I. J. Inorg. Biochem. 2000, 78, 79.
- (6) Pierpont, C. G. Coord. Chem. Rev. 2001, 216-217, 99.
- (7) Gütlich, P.; Garcia, Y.; Woike, T. Coord. Chem. Rev. 2001, 219–221, 839.

(8) Sato, O.; Hayami, S.; Gu, Z.-z.; Takahashi, K.; Nakajima, R.; Fujishima, A. *Chem. Phys. Lett.* **2002**, 355, 169.

(9) Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. Angew. Chem. Int. Ed. 2003, 32, 880.

(10) Liu, H. W.; Matsuda, K.; Gu, Z. Z.; Takahashi, K.; Cui, A. L.; Nakajima, R.; Fujishima, A.; Sato, O. *Phys. Rev. Lett.* **2003**, *90*, 167403.

(11) Dei, A. Angew. Chem. Int. Ed. 2005, 44, 1160.

(12) Goujon, A.; Gillon, B.; Debede, A.; Cousson, A.; Gukasov, A.; Jeftic, J.; McIntyre, G. J.; Varret, F. *Phys. Rev. B* **2006**, *73*, 104413.

(13) Sato, O.; Tao, J.; Zhang, Y.-Z. Angew. Chem. Int. Ed. 2007, 46, 2152.

(14) Kahn, O.; Launay, J. P. Chemtronics 1988, 3, 140.

(15) Elsner, O.; Ruiz-Molina, D.; Vidal-Gancedo, J.; Rovira, C.; Veciana, J. Chem. Commun. **1999**, 579.

- (16) Elsner, O.; Ruiz-Molina, D.; Ratera, I.; Vidal-Gancedo, J.; Rovira, C.; Veciana, J. J. Organomet. Chem. **2001**, 637–639, 251.
- (17) Ratera, I.; Ruiz-Molina, D.; Renz, F.; Ensling, J.; Wurst, K.; Rovira, C.; Gütlich, P.; Veciana, J. J. Am. Chem. Soc. 2003, 125, 1462.
- (18) Ratera, I.; Sporer, C.; Ruiz-Molina, D.; Ventosa, N.; Baggerman, J.; Brouwer, A. M.; Rovira, C.; Veciana, J. J. Am. Chem. Soc. 2007, 129,
- 6117. (19) Ballester, M.; Riera, J.; Castañer, J.; Badía, C.; Monsó, J. M. *J.*

Am. Chem. Soc. 1971, 93, 2215.
(20) Lloveras, V.; Vidal-Gancedo, J.; Ruiz-Molina, D.; Figueira-Duarte, T. M.; Nierengarten, J.-F.; Veciana, J.; Rovira, C. Faraday

Duarte, I. M.; Nierengarten, J.-F.; Veciana, J.; Kovira, C. Faraday Discuss. 2006, 131, 291.

(21) Sporer, C.; Ratera, I.; Ruiz-Molina, D.; Vidal-Gancedo, J.; Wurst, K.; Jaitner, P.; Rovira, C.; Veciana, J. *J. Phys. Chem. Solids* **2004**, *65*, 753.

(22) Sporer, C.; Ratera, I.; Ruiz-Molina, D.; Zhao, Y.; Vidal-Gancedo, J.; Wurst, K.; Jaitner, P.; Clays, K.; Persoons, A.; Rovira, C.; Veciana, J. *Angew. Chem. Int. Ed.* **2004**, *43*, 5266.

- (23) D'Avino, G.; Grisanti, L.; Guasch, J.; Ratera, I.; Veciana, J.; Painelli, A. J. Am. Chem. Soc. **2008**, 130, 12064.
- (24) Painelli, A.; Terenziani, F. J. Am. Chem. Soc. 2003, 125, 5624.
- (25) Terenziani, F.; Painelli, A. Phys. Rev. B **2003**, 68, 165405.
- (26) Kondo, M.; Uchikawa, M.; Namiki, K.; Zhang, W.-W.; Kume, S.;
- Nishibori, E.; Suwa, H.; Aoyagi, S.; Sakata, M.; Murata, M.; Kobayashi,
- Y.; Nishihara, H. J. Am. Chem. Soc. 2009, 131, 12112. Kondo, M.;
- Uchikawa, M.; Zhang, W.-W.; Namiki, K.; Kume, S.; Murata, M.;

Kobayashi, Y.; Nishihara, H. Angew. Chem. Int. Ed. 2007, 46, 6271. (27) Rovira, C.; Ruiz-Molina, D.; Elsner, O.; Vidal-Gancedo, J.;

- Bonvoisin, J.; Launay, J.-P.; Veciana, J. Chem. Eur. J. 2001, 7, 240.
- (28) Zou, C.; Wrighton, M. S. J. Am. Chem. Soc. 1990, 112, 7578.
- (29) Wadswort, W. S., Jr.; Emmons, W. D. J. Am. Chem. Soc. 1961, 83, 1733.
- (30) Grisanti, L.; D'Avino, G.; Painelli, A.; Guasch, J.; Ratera, I.; Veciana, J. *J. Phys. Chem. B* **2009**, *113*, 4718.

(31) Miravitlles, C.; Molins, E.; Solans, X.; Germain, G.; Declercq, J. P. J. Incl. Phenom. **1985**, 3, 27. Veciana, J.; Riera, J.; Castañer, J.; Ferrer, N. J. Organomet. Chem. **1985**, 297, 131. Molins, E.; Mas, M.; Maniukiewicz, W.; Ballester, M.; Castañer, J. Acta Cryst. C **1996**, 52, 2412. Guasch, J.; Fontrodona, X.; Ratera, I.; Rovira, C.; Veciana, J. Acta Cryst. C **2013**, DOI: 10.1107/S0108270113002072.

- (32) Painelli, A.; Terenziani, F. J. Phys. Chem. A **2000**, 104, 11041. Terenziani, F.; Painelli, A.; Comoretto, D. J. Phys. Chem. A **2000**, 104, 11049
- (33) Terenziani, F.; Painelli, A.; Girlando, A.; Metzger, R. M. J. Phys. Chem. B 2004, 108, 10743.

(34) Boldrini, B.; Cavalli, E.; Painelli, A.; Terenziani, F. J. Phys. Chem. A 2002, 106, 6286.

(35) Grisanti, L.; Sissa, C.; Terenziani, F.; Painelli, A.; Roberto, D.; Tessore, F.; Ugo, R.; Quici, S.; Fortunati, I.; Garbin, E.; Ferrante, C.; Bozio, R. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9450.

(36) Painelli, A. Chem. Phys. 1999, 245, 185.

(37) Painelli, A.; Terenziani, F.; Angiolini, L.; Benelli, T.; Giorgini, L. Chem. Eur. J. 2005, 11, 6053.

(38) Terenziani, F.; D'Avino, G.; Painelli, A. ChemPhysChem 2007, 8, 2433.

(39) Todescato, F.; Fortunati, I.; Carlotto, S.; Ferrante, C.; Grisanti, L.; Sissa, C.; Painelli, A.; Colombo, A.; Dragonetti, C.; Roberto, D. *Phys. Chem. Chem. Phys.* **2011**, *13*, 11099.

- (40) Grisanti, L.; Terenziani, F.; Sissa, C.; Cavazzini, M.; Rizzo, F.; Orlandi, S.; Painelli, A. J. Phys. Chem. B **2011**, 115, 11420.
- (41) Girlando, A.; Sissa, C.; Terenziani, F.; Painelli, A.;
- Chwialkowska, A.; Ashwell, G. J. ChemPhysChem 2007, 8, 2195.

(42) Stewart, J. J. P. J. Mol. Model. 2007, 13, 1173.

- (43) Stewart, J. J. P. MOPAC2007; Stewart Computational Chemistry, Colorado Springs, CO, http://OpenMOPAC.net.
- (44) Guasch, J.; Grisanti, L.; Lloveras, V.; Vidal-Gancedo, J.; Souto, M.; Morales, D. C.; Vilaseca, M.; Sissa, C.; Painelli, A.; Ratera, I.;