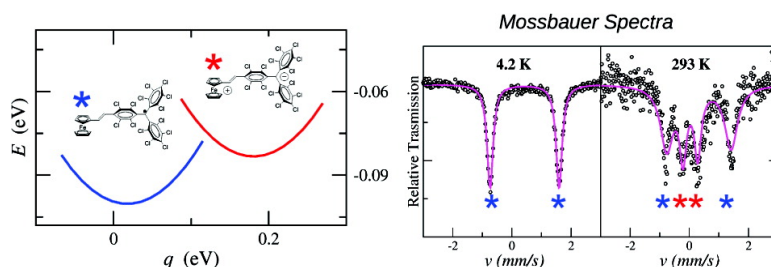Article

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Bistability in Fc-PTM Crystals: The Role of Intermolecular Electrostatic Interactions

Gabriele D'Avino,[†] Luca Grisanti,[†] Judith Guasch,[‡] Imma Ratera,[‡] Jaume Veciana,[‡] and Anna Painelli*,[†]

Dipartimento Chimica GIAF, Parma University and INSTM-UdR Parma, I-43100 Parma, Italy, and Institut de Ciéncia de Materials de Barcelona (CSIC)/CIBER-BBN, Campus University Bellaterra, 08193-Cerdanyola, Barcelona, Spain

Received April 25, 2008; E-mail: anna.painelli@unipr.it

Abstract: Fc-PTM is a valence tautomeric radical, where the ferrocene (Fc) group, a good electron donor, is linked by an ethylenic spacer to a perchlorotriphenylmethyl radical (PTM•), a good electron acceptor. In solution this compound exists mainly in the neutral Fc-PTM• form which can be photoexcited through an intramolecular electron transfer to the zwitterionic Fc$^{+•}$-PTM$^-$ form. By contrast, in crystals of Fc-PTM at room temperature both the neutral and the zwitterionic forms coexist, pointing to a true bistability phenomenon. We rationalize these findings accounting for the role of intermolecular electrostatic interactions in Fc-PTM crystals. In fact the energy of the zwitterionic Fc$^{+•}$-PTM$^-$ form is lowered in the crystal by attractive electrostatic intermolecular interactions and the cooperative nature of these interactions explains the observed coexistence of neutral Fc-PTM• and zwitterionic Fc$^{+•}$-PTM$^-$ species. The temperature evolution of Mössbauer spectra of Fc-PTM is quantitatively reproduced adopting a bottom-up modeling strategy that combines a molecular model, derived from optical spectra of Fc-PTM in solution, with a model for intermolecular electrostatic interactions, supported by quantum-chemical calculations. Fc-PTM then offers the first experimental demonstration of bistability induced by electrostatic interactions in crystals of valence tautomeric donor−acceptor molecules.

Introduction

Bistability is a rare phenomenon in molecular materials that fascinates molecular and material scientists both in view of its applicative potential and, on a more fundamental vein, as the extreme result of cooperative intermolecular interactions.[1,2] A comprehensive picture of the molecular and supramolecular physics of the system is required to understand bistability in molecular materials. Gas phase or solvated molecules having two (or more) thermally accessible stable states show intriguing pseudobistable (or multistable) behavior. Thus, mixed valence molecules and valence tautomeric complexes offer intriguing examples of molecules that in solution equilibrate between two different forms, whose relative population can be tuned by changing external conditions.[1,3] In the lack of cooperative interactions however the exchange between the two forms is fast, and, while interesting from a fundamental point of view, pseudobistability in solution is not immediately interesting for applications.[1]

Cooperative intermolecular interactions may lead to true bistability (or multistability) in the solid state. In fact in truly bistable (multistable) systems two (or more) *long-lived* stable states are accessible to the system. Interconversion between the stable forms is extremely slow in the solid state because it implies changing the state of a large number of molecules at a time. Bistability always accompanies first-order phase transitions

† Parma University.
‡ Institut de Ciéncia de Materials de Barcelona.

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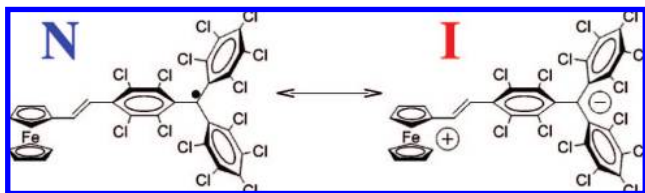
Figure 1. Neutral (DA$^\bullet$) and zwitterionic (D$^{+\bullet}$A$^-$) resonating structures of Fc-PTM.

and shows up with hysteresis loops and/or with the appearance of coexisting phases.[4] Resulting from cooperative interactions, bistability is a nonlinear phenomenon whose modeling requires a detailed understanding of supramolecular interactions in the solid-state.[1,2]

In traditional molecular crystals intermolecular interactions are weak, and hardly support bistability. Most often a variation of the lattice and/or molecular geometry in the two phases is invoked as a primary cause of cooperativity, with phonons and related internal pressure effects playing a major role. Vibrational degrees of freedom are good candidates to explain bistability in spin crossover systems.[2a,d] However, in molecular materials where bistability is associated with charge-transfer degrees of freedom (i.e., in systems, like valence tautomers, where a different charge distribution characterizes the two stable states), electrostatic intermolecular forces represent an additional powerful source for cooperative interactions.[5,6]

Fc-PTM belongs to an interesting family of valence tautomeric molecules based on the ferrocene (Fc) group, as a good electron donor (D) unit.[7−9] In Fc-PTM the Fc group is linked by an ethylenic spacer to a perchlorotriphenylmethyl radical (PTM$^\bullet$), a good electron acceptor (A). As shown in Figure 1, Fc-PTM resonates between a neutral (DA$^\bullet$) and a zwitterionic form (D$^{+\bullet}$A$^-$). Absorption spectra of Fc-PTM in solution show a band in the infrared region assigned to an intramolecular electron transfer between D and A$^\bullet$ units.[9] This band shows a positive solvatochromic shift (the band maximum shifts from 892 nm in *n*-hexane to 1003 nm in DMSO) demonstrating that in solution Fc-PTM can be described as a largely neutral DA$^\bullet$ dye.[10] The zwitterionic D$^{+\bullet}$A$^-$ form, reached upon photoexcitation, is more than 1 eV higher in energy.[9] In the crystalline phase however Mössbauer spectra demonstrate that both the neutral and zwitterionic forms of Fc-PTM are long-lived states that are thermally populated at ambient temperature.[8] Therefore, such results show that Fc-PTM is a bistable system in which cooperative intermolecular interactions are operative. Here we rationalize these findings accounting for the role of intermolecular electrostatic interactions in Fc-PTM crystals. In fact, the energy of the zwitterionic Fc$^{+\bullet}$-PTM$^-$ form can be lowered by

attractive electrostatic intermolecular interactions in the lattice, and, what is even more important, the cooperative nature of these interactions explains the observed coexistence of neutral Fc-PTM$^\bullet$ and zwitterionic Fc$^{+\bullet}$-PTM$^-$ species in terms of electrostatically induced bistability. We fully exploit the molecular nature of Fc-PTM crystals and adopt a bottom-up modeling strategy[12] that combines a molecular model, derived from optical spectra of Fc-PTM in solution, with a model for intermolecular electrostatic interactions, supported by quantum-chemical calculations. This model is validated via a quantitative comparison with temperature-dependent Mössbauer spectra. Fc-PTM then offers the first experimental demonstration of bistability induced by electrostatic interactions in crystals of valence tautomeric DA molecules.

The paper is organized as follows. In section I we derive an essential state model for Fc-PTM from the detailed analysis of its solution spectra. Adopting an approach that has been developed and successfully applied for closed-shell DA chromophores (also called push−pull chromophores), we extract an environment-independent model for Fc-PTM that will be used to build up a model for Fc-PTM crystals, as described in section III. In section II we summarize the model for electrostatic interactions in crystals of DA molecules and discuss the conditions required for observing bistability. Then in section III we develop the specific model for Fc-PTM crystals combining the molecular model extracted from solution spectra with a model for electrostatic intermolecular interactions supported by quantum chemical calculation. Finally, section IV presents a discussion of the results and the most important conclusions.

I. The Molecular Model for Fc-PTM from Solution Spectra

The low-energy physics of Fc-PTM is governed by the DA$^\bullet$ ↔ D$^{+\bullet}$A$^-$ resonance shown in Figure 1. In close analogy with closed shell DA chromophores,[11] we then describe the Fc-PTM radical in terms of a minimal model that just accounts for two essential electronic states, $|DA^\bullet\rangle$ and $|D^{+\bullet}A^-\rangle$, corresponding to the two resonating structures in Figure 1. The relevant Hamiltonian is given by[11a−c]

$$\hat{h} = 2z\hat{\rho} - \tau(|DA^\bullet\rangle\langle D^{+\bullet}A^-| + |D^{+\bullet}A^-\rangle\langle DA^\bullet|) \quad (1)$$

where $\hat{\rho} = |D^{+\bullet}A^-\rangle\langle D^{+\bullet}A^-|$ is the ionicity operator, $2z$ is the ionization energy, that is, the energy gap between the two basis states, and τ is the hybridization energy, corresponding to the matrix element that mixes the two basis states. The diagonalization of the two state Hamiltonian leads to a ground and an excited state:

$$|G\rangle = \sqrt{1-\rho}|DA^\bullet\rangle + \sqrt{\rho}|D^{+\bullet}A^-\rangle$$
$$|E\rangle = \sqrt{\rho}|DA^\bullet\rangle - \sqrt{1-\rho}|D^{+\bullet}A^-\rangle \quad (2)$$

defined in terms of a single parameter $\rho = \langle G|\hat{\rho}|G\rangle = (1 - z/\sqrt{(z^2 + t^2)})/2$ that measures the molecular ionicity, that is,

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the fraction of electron transferred from the D to the A$^\bullet$ unit in the ground state, or, equivalently, the fraction of unpaired spin on the Fc fragment. For positive z the ground-state is neutral, $\rho < 0.5$, and becomes ionic (or zwitterionic), $\rho > 0.5$, for negative z. At the neutral−ionic interface, $z = 0$, the two basis states have equal weights in the ground-state and $\rho = 0.5$. For small hybridization energy, $\tau \ll |z|$, the mixing between the two basis states stays small and the system is either largely neutral ($\rho \approx 0$) or largely zwitterionic ($\rho \approx 1$) for positive or negative z, respectively. On the opposite side, a large hybridization energy, $\tau \gg |z|$ implies a large mixing between the basis states and $\rho \approx 0.5$.[11a−c]

The $| D^{+\bullet}A^- \rangle$ state is characterized by a large dipole moment μ_0, so that all other matrix elements of the dipole moment operator on the chosen basis can be neglected.[13] With this approximation all quantities of spectroscopic interest are written as a function of the molecular ionicity, ρ: the transition frequency $\omega_{CT} = \tau/\sqrt{(\rho(1 - \rho))}$ (units with $\hbar = 1$) is minimal at $\rho = 0.5$, where the transition dipole moment $\mu_{CT} = \mu_0\sqrt{(\rho(1 - \rho))}$ is highest.[11c] Moreover, for neutral systems, $\rho < 0.5$, the charge transfer (CT) transition goes from the ground-state with a small dipole moment, $\mu_G = \mu_0\rho$, toward the excited-state with a large dipole moment $\mu_E = \mu_0(1 - \rho)$. Polar solvents stabilize polar states, and for neutral molecules a red-shift of the absorption band with an increase in the solvent polarity is observed, while the opposite occurs for zwitterionic dyes ($\rho > 0.5$).[11b] More generally, the solvatochromism of polar dyes gives information on the molecular properties, and in recent years a method has been proposed to extract reliable and *solvent-independent* molecular parameters from the analysis of solution spectra. The details of the model can be found in the literature,[11] and its basic features are summarized hereafter.

The polarization of the solvent that surrounds a polar solute generates at the solute location an electric field, called the reaction field F_R, proportional to the solute dipole moment. This electric field lowers the energy of the $| D^{+\bullet}A^- \rangle$ state. Two different contributions to F_R can be recognized.[11b] The first one is due to the polarization of the electronic clouds of the solvent molecules. This electronic contribution to F_R is characterized by a fast dynamics with respect to the time-scale of the charge resonance and, as such, it enters the model with a renormalization of the molecular parameters τ and z. The electronic polarization is described by the solvent refractive index and in view of the marginal variability of the refractive index in different solvents and/or in molecular crystals, we consider z and τ as solvent-independent molecular parameters, also applicable to molecular crystals.[11b] The second contribution to the reaction field arises from the reorientation of *polar* solvent molecules around the polar solute.[11b] The orientational contribution to the reaction field, F_{or}, is slow with respect to CT degrees of freedom, and must be explicitly accounted for. Treating the solvent as a continuum elastic medium, a single parameter, the solvent relaxation energy, ϵ_{or}, defines polar solvation. It measures the decrease of the $|D^{+\bullet}A^-\rangle - |DA^\bullet\rangle$ gap as a result of the reorientation of the solvent and depends on solvent properties (refractive index and dielectric constant) but also on the shape and dimensions of the solute. A priori estimates of ϵ_{or} are delicate, and we treat it as an adjustable parameter.[11b] Polar solvation affects the frequency of the CT transition and leads to inhomogeneous broadening of optical spectra.[11b−e]

Molecular vibrations are coupled to electronic degrees of freedom and are responsible for the appearance in electronic spectra of the so-called vibronic structure. To keep the model simple we introduce a harmonic vibrational coordinate Q with frequency ω and assume that two different equilibrium positions are associated to the two basis states.[11a] The ionization gap, $2z$, then acquires a linear dependence on Q given by $2z(Q) = 2z(0) - \omega Q\sqrt{(2\varepsilon_v)}$, where ε_v is the vibrational relaxation energy. With these basic ingredients the evolution of absorption and fluorescence spectra of DA chromophores can be understood quite naturally, and optical spectra of several closed-shell DA dyes have already been quantitatively reproduced along these lines.[11c−e,12a]

The proposed approach, accounting for both solvation and vibrational couplings, closely resembles the famous Marcus and Marcus−Hush models.[14] However it differs from the Marcus approach in a major way: the parameters entering our model refer to the basis states (sometimes called the diabatic states) and not to the ground and excited states of the system (the so-called adiabatic states), as in the Marcus approach. The polarity of the ground and excited states, that is, the nature of the states actually involved in the transition, evolves with the solvent polarity, and the parameters entering the Marcus model are intrinsically *solvent dependent*. In our model instead the ground and excited states are calculated as solvent-dependent combinations of the two basis states:[11] our model parameters refer to the basis states and, as such, they are not affected by the solvent polarity. The evolution of optical spectra with the solvent polarity and the corresponding evolution of the Marcus model parameters stem out naturally from the evolution of the mixing of the ground and excited states as driven by the lowering of the energy of $D^{+\bullet}A^-$ state in polar solvents. Therefore, in our model the solvatochromism of optical spectra of DA chromophores can be quantitatively reproduced in terms of a few rigorously *solvent-independent* molecular parameters, while tuning only ε_{or} to account for the solvent polarity.[11] This has two main consequences: (a) an important reduction of the number of fitting parameters, and (b) the definition of a set of *environment-independent molecular parameters* that may be transferred to model the same molecule in different environments, like in the solid state.

The model works properly for Fc-PTM, as shown in Figure 2 where experimental spectra (from ref 9) are compared with spectra calculated with the molecular parameters in Table 1, and with ε_{or} increasing from 0 in cyclohexane up to 0.6 eV in DMSO. Both the hybridization energy, τ, and the strength of vibrational coupling, ε_v, are small in Fc-PTM if compared with typical values for closed-shell DA dyes.[11,12] The radical nature of Fc-PTM explains the small electron-vibration coupling since transferring an electron from the D the A$^\bullet$ site has minor effects on the molecular geometry if compared with the large reorganization of bond lengths expected and observed for closed-shell DA chromophores.[15]

The molecular model for Fc-PTM was derived from optical spectra, but a comparison with electrochemistry data can be attempted. The energy required to turn a neutral DA$^\bullet$ molecule

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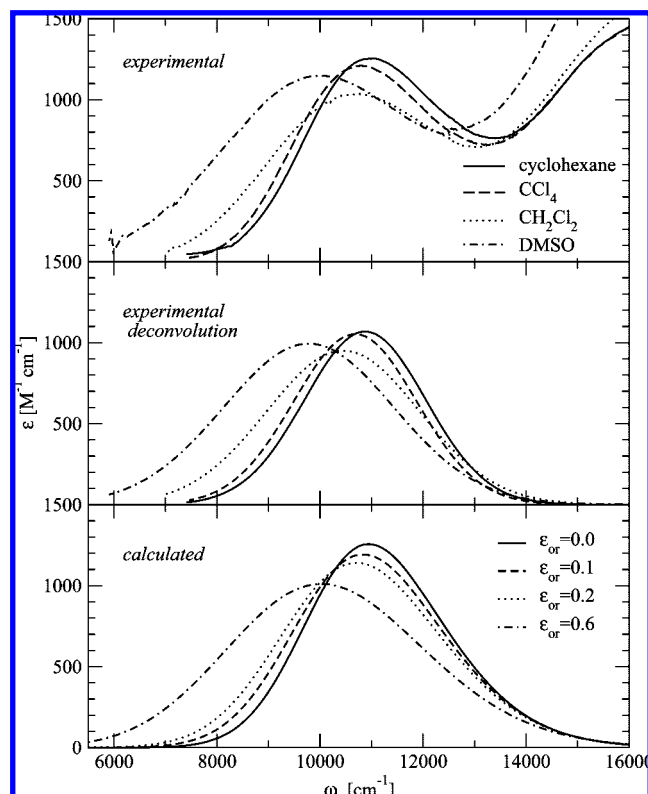
Figure 2. Absorption spectra of Fc-PTM in several solvents: (top panel) raw experimental spectra from ref 9; (central panel) deconvolution of the experimental lowest energy bands; (bottom panel) spectra calculated with the molecular parameters in Table 1, imposing a Gaussian line shape to each vibronic line with full-width at half-maximum 0.32 eV, independent of the solvent. The ϵ_{or} values optimized for the different solvents are shown in the figure (eV units).

Table 1. Molecular Parameters (eV Units) for the Two-State Model of Fc-PTM

z	τ	ϵ_v	ω
0.61	0.35	0.10	0.18

into a fully equilibrated $D^{+\bullet}A^-$ molecule in solution is, in our model, $2z - \epsilon_v - \epsilon_{or}$. The resulting values 0.92 and 0.52 eV in CH_2Cl_2 and DMSO, respectively, compare favorably with the ΔE_{redox} measured in ref 9 from cyclic voltammetry data, ΔE_{redox} = 0.764 V in CH_2Cl_2 and ΔE_{redox} = 0.576 V in acetonitrile, a solvent with a similar polarity as DMSO. More detailed and reliable comparisons are however hindered by the need to correct the ΔE_{redox} estimate for contributions accounting for the intramolecular electrostatic interaction between positive and negative charges in the $D^{+\bullet}A^-$ state,[9] as well as for contributions due to the hybridization of D and A orbitals (as originating from the finite τ) and hence to the partial delocalization of the positive (negative) charge in the A (D) molecular fragment in the D^+A (DA^-) molecular ions whose energy is actually measured in the voltammetry experiment.

II. Cooperative Electrostatic Interactions in Molecular Crystals

Intermolecular distances in Fc-PTM crystals are sufficiently large to neglect intermolecular charge-transfer processes. Consequently, the minimal model for the crystal describes a 3-dimensional arrangement of DA$^\bullet$ molecules interacting only via electrostatic forces.[5,6] To start with, let us consider the limit

$\tau = 0$, so that each molecule can either be in the $|DA^\bullet\rangle$ or $|D^{+\bullet}A^-\rangle$ state, with energy 0 and $2z$, respectively. In the reasonable hypothesis that electrostatic interactions among neutral molecules are negligible, the energy required to switch N molecules from the neutral to the zwitterionic state is $2Nz$ for noninteracting molecules but becomes $2N(z + M)$ in the lattice, where $2M$ is the Madelung energy of a lattice of fully ionic $D^{+\bullet}A^-$ molecules. The intermolecular electrostatic energy, M, is given by

$$M = \frac{1}{2N}\sum_{ij} V_{ij} \tag{3}$$

with V_{ij} measuring the electrostatic interaction between two fully ionic ($\rho = 1$) molecules at sites i and j. M is negative for attractive intermolecular interactions: for $z + M > 0$ the ground-state of the system corresponds to a collection of neutral molecules, while for $z + M < 0$ it corresponds to a collection of zwitterions. In other terms, the ground-state of the crystal is defined by the competition of the *on-site energy*, z, and of the *intermolecular electrostatic energy*, M. This competition is the key point for bistability.

This picture is however too simple since finite τ values must be introduced to describe molecules with fractional ρ, and hence to account for the sizable intensity of intramolecular charge-transfer bands. Only intramolecular electron-hopping is allowed in our model,[5,6] so that electrons are strictly localized within each molecular unit. Adopting a bottom-up modeling strategy,[5,6,12] we then rewrite the Hamiltonian of the crystal, $\hat{H}$, as the sum of molecular Hamiltonians plus a term that accounts for classical electrostatic interactions:

$$\hat{H} = \sum_i \hat{h}_i + \frac{1}{2}\sum_{i,j} V_{ij}\hat{\rho}_i\hat{\rho}_j \tag{4}$$

where $\hat{h}_i$ is the molecular Hamiltonian in eq 1, relevant to the i-th molecule, V_{ij} is the electrostatic interaction between two zwitterionic molecules at sites i,j, and $\hat{\rho}_i$ is the ionicity operator for the i-th molecule.

The Hamiltonian in eq 4 can be diagonalized exactly on clusters of N molecules,[5] but since the basis increases as 2^N, it is impossible to obtain exact results on large enough three-dimensional clusters as required to understand the role of long-range electrostatic interactions. We therefore adopt the mean field (mf) approximation,[5,6,16] a good and powerful approximation to describe the ground-state properties of the system. In the mf approximation the Hamiltonian for interacting molecules reduces to the sum of effective molecular Hamiltonians, as follows:

$$\hat{H} = \sum_i \hat{h}_i^{mf} - NM\rho^2 \tag{5}$$

where $\hat{h}_i^{mf}$ is the two-state Hamiltonian in eq 1, but with z renormalized to define an effective ionization energy: $z_{eff} = z + M\rho$, where $\rho = \langle\hat{\rho}_i\rangle$ is the ionicity of the molecule in the crystal (we consider a crystal of equivalent molecules). In other terms, the energy required to ionize a DA$^\bullet$ molecule to the $D^{+\bullet}A^-$ state is $2z$ for isolated molecules (more precisely for molecules in a nonpolar solvent) but in the crystal this energy becomes $2z_{eff}$, and it depends on ρ because each molecule interacts with surrounding molecules, whose charge distribution is defined by ρ.[5,6,16] Attractive interactions ($M < 0$) decrease

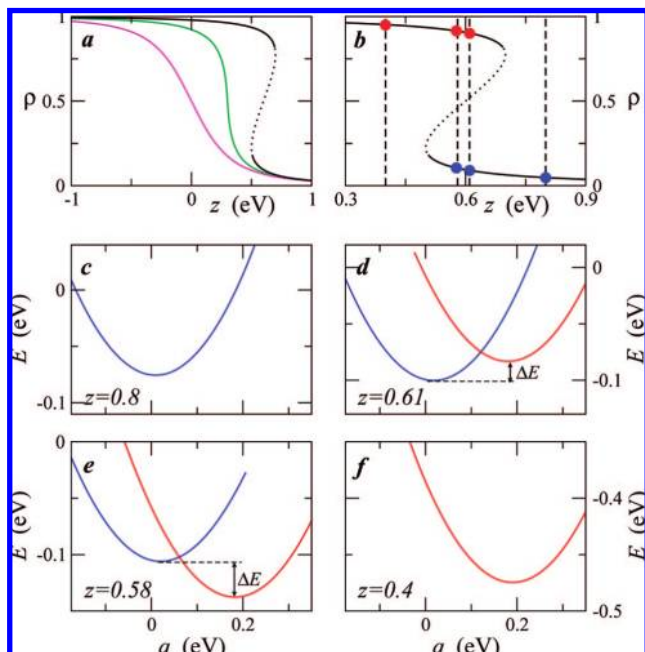(16) Soos, Z. G.; Keller, H. J.; Moroni, W.; Nothe, D. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 442.

Figure 3. (a) $\rho(z)$ curves calculated for $\tau = 0.35$ eV and different M. Magenta, green, and black curves refer to M = 0, −0.6, and −1.2 eV, respectively. For $M = -1.2$ the region of the $\rho(z)$ curve with positive slope (marked by the dotted line) corresponds to unstable solutions. (b) Enlarged view of the $M = -1.2$ eV curve in the bistability region. Vertical dashed lines mark the values $z = 0.8$, 0.61, 0.58, and 0.40 eV, whose potential energy surfaces (PES) are shown in panels c−f. Blue and red dots mark stable neutral and zwitterionic states, respectively. (c−f) Ground-state PESs corresponding to the states marked by dots in panel b. Specifically the PES values are calculated for $\tau = 0.35$ eV, $M = -1.1$ eV $\varepsilon_v = 0.10$ eV (so that $M - \varepsilon_v = -1.2$ eV), and the z values shown in each panel. Blue and red lines are used for neutral and ionic states, respectively.

the effective ionization energy, favoring ionic lattices. Moreover, the self-consistent nature of the mf Hamiltonian, with the ionization energy in the crystal, $2z_{eff}$, depending on the average molecular ionicity ρ, captures the cooperative nature of intermolecular interactions. The result of the complex interplay of these factors is summarized in Figure 3a that shows the $\rho(z)$ curves calculated for molecular crystals with $\tau = 0.35$ (as relevant for Fc-PTM) and different M. For not-too-large $|M|$ a smooth crossover is observed from a largely neutral regime ($\rho \approx 0$) to a largely ionic regime ($\rho \approx 1$): in other terms, for small $|M|$ a region is found where the hybridization energy, τ, is large enough to stabilize states with $\rho \approx 0.5$. On the opposite side, when $|M| > 2\tau$ the hybridization energy is never dominant, and states with $\rho \approx 0.5$ are not accessible: the charge crossover becomes discontinuous.[5,6,16] This is illustrated by the $M = -1.2$ eV curve in Figure 3a (and its enlarged view in Figure 3b) where the portion of the $\rho(z)$ curve with positive slope corresponds to unstable states. In other words, for the parameters in the figure and $M = -1.2$ eV states with ionicities $0.18 < \rho < 0.82$ are forbidden. More interesting for our discussion is however the appearance of a bistability region where, for each z value, two different stable states with $\rho \approx 0$ and $\rho \approx 1$ are found. This bistability, induced by electrostatic intermolecular interactions, is the key to explain experimental observations on Fc-PTM crystals.

The coupling between electronic and vibrational degrees of freedom is small in Fc-PTM and could be disregarded. However a more immediate understanding of bistability is obtained if molecular vibrations are explicitly accounted for. As discussed in the previous section, we account for a vibrational coordinate

Q on each molecule. To simplify notation we introduce here an auxiliary molecular coordinate $q_i = \omega Q_i \sqrt{(2\varepsilon_v)}$. With this definition the mf Hamiltonian in eq 5 becomes

$$\hat{H} = \sum_i \hat{h}_i^{mf}(q_i) - NM\rho^2 + \sum_i \frac{1}{4\varepsilon_v} q_i^2 \qquad (6)$$

where the last term is the vibrational potential energy (the vibrational kinetic energy is disregarded in the adiabatic approximation), and $\hat{h}_i^{mf}(q_i)$ is the q_i-dependent mf Hamiltonian for the ith molecule. This molecular Hamiltonian again coincides with the two-state Hamiltonian in eq 1 but with a q_i-dependent z_{eff}, such as $z_{eff} = z + M\rho - q_i/2$.[12a] By substituting q_i with its equilibrium value, $(q_i)_{eq} = 2\varepsilon_v\rho$, we get a simple expression for the effective ionization energy, $2z_{eff} = 2[z + (M - \epsilon_v)\rho]$, accounting for both electrostatic intermolecular interactions and molecular vibrations. The coupling between electronic and vibrational degrees of freedom plays the same role as *attractive* electrostatic intermolecular interactions.[17] The $\rho(z)$ curves in Figure 3, panel a, then also apply in the presence of vibrational coupling, but with M replaced by $M - \varepsilon_v$. For Fc-PTM $\varepsilon_v \sim 0.1$ eV and the vibrational contribution to M represents just a minor correction.

More interesting is the calculation of the q_i-dependent ground-state energy, obtained by the diagonalization of the q_i-dependent mf Hamiltonian in eq 6. Panels c−f of Figure 3 show the ground-state potential energy surfaces (PES) calculated for a system with $\tau = 0.35$ eV $\varepsilon_v = 0.1$ eV, as relevant for Fc-PTM, and $M = -1.1$ eV (so that $M - \varepsilon_v = -1.2$ eV, corresponding to the black $\rho(z)$ curve in Figure 3b). For large and positive ionization gap, $z = 0.8$ eV, the $\rho(z)$ curve in Figure 3b leads to a single solution corresponding to a largely neutral ground state with $\rho \approx 0.05$. The corresponding PES in Figure 3c is almost harmonic with a minimum located at the equilibrium ($q = 2\rho\varepsilon_v \approx 0.01$ eV). Similarly, for $z = 0.4$ (corresponding to a large and negative z_{eff}) a single ρ value is found, corresponding to a largely ionic state with $\rho = 0.95$. The corresponding PES in Figure 3f is centered at $q \approx 0.19$ eV. For z values in the bistability region two stable states, with different ρ, are found. For $z = 0.61$, states with $\rho = 0.09$ and 0.91 are both stable. The corresponding PES values in Figure 3d are almost harmonic with minima located at $q \approx 0.018$ and 0.18 eV. Of course just one of the two states, the lowest energy one with $\rho = 0.09$, is thermodynamically stable, while the $\rho = 0.91$ state is a metastable state. For $z = 0.58$ eV (cf Figure 3e), again in the bistability region, the situation is reversed with the stable state corresponding to a largely ionic state ($\rho = 0.9$) while the metastable state corresponds in this case to a largely neutral state ($\rho = 0.1$).

It is important to realize that all the curves in Figure 3c−f describe *ground-state* PESs. In fact they have been obtained in the mf approximation searching for the lowest energy state for each geometrical and charge configuration. Specifically, the two PESs in panel 3d (or in 3e) correspond to the two different ground states accessible to the crystal in the bistability region. The blue curve describes the almost neutral ($\rho \approx 0$) ground-state accessible to a molecule in a crystal of almost neutral molecules, while the red curve describes the almost zwitterionic ($\rho \approx 1$) ground-state relevant to a molecule in a crystal of almost zwitterionic molecules. These *ground-state* PESs do not offer any spectroscopically relevant information because transitions between the two PESs would imply a change in the ionicity of

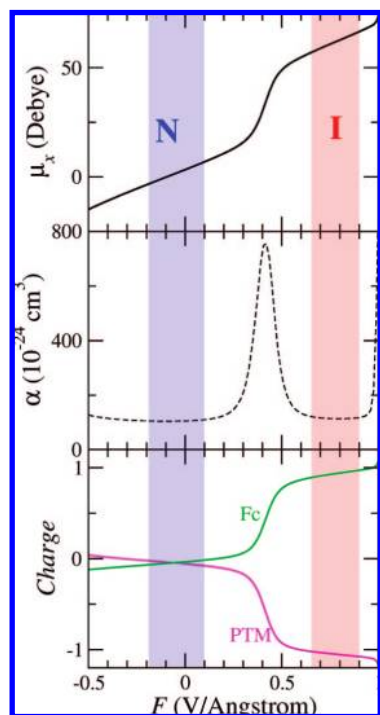(17) Painelli, A.; Girlando, A. *Phys. Rev. B* **1988**, *37*, 5748.

Figure 4. Results of PM6 calculations for Fc-PTM under an external static electric field, F. Field-dependence of the molecular dipole moment μ_x (top panel), molecular polarizability α (central panel), and total net charges on the Fc and PTM units (bottom panel). Blue and red shadowed regions approximately mark the neutral and the ionic regimes, corresponding to flat regions of $\alpha(F)$.

all the molecules in the crystals and could not be directly induced by photon absorption. Photon absorption is in fact a *vertical* process corresponding to the excitation of one or at most a few molecules:[5a] the PESs in Figure 3 do not describe vertical excited states. Photoinduced phase transitions are an intriguing possibility for bistable systems that can be driven from the stable to the metastable PES. In this case however the transition between the two stable states (i.e., between the two PESs in Figure 3d and e) would occur as a result of a cascade of electron-transfer processes first induced by the vertical absorption of a photon.

III. Electrostatic Interactions in Fc-PTM: A Key to Bistability

Results in Figure 3 demonstrate that a discontinuous neutral to ionic crossover can be induced in crystals of DA chromophores by electrostatic intermolecular interactions, and that for the molecular parameters relevant to Fc-PTM the corresponding bistability region can be fairly large. In the spirit of the bottom-up approach,[5,6,12] all molecular parameters entering the mf Hamiltonian in eq 6 are fixed by the analysis of solution spectra of Fc-PTM, in the reasonable approximation that the two-state model that describes Fc-PTM in solution also applies to Fc-PTM crystals. To support our hypothesis of electrostatically induced bistability in Fc-PTM crystals we then only need estimates of M, defined in eq 2 as half-the Madelung energy of a lattice of *zwitterionic* $D^{+}A^{-}$ molecules. In the simplest approximation[5,6,12] M can be estimated modeling the charge distribution on a zwitterion in terms of a positive and a negative electron charge located at the center of the D and A sites, respectively. In this approximation, and locating the charges at the positions of the Fe atom and of the central C-atom of the

PTM unit, we estimate $M = -0.75$ eV, an encouraging result. However this approximation is too crude for large molecules as Fc-PTM. An improved estimate of M can be obtained modeling the charge distribution on each molecule as a collection of point atomic charges as estimated by quantum chemical calculations.[18] The calculation is not trivial, however, because we need intermolecular electrostatic interactions among Fc-PTM molecules in the zwitterionic $D^{+\bullet}A^{-}$ form, and not in the almost neutral ground state that results from gas-phase calculations. To overcome this subtle problem we perform calculations on a molecule subject to an external static electric field as to force the charge transfer from the D to the $A^{\bullet}$ unit.

Figure 4 summarizes the results of restricted Hartree–Fock PM6 calculations (MOPAC2007 package)[19] on an Fc-PTM molecule in the experimental crystallographic geometry.[20] A static electric field F is directed along the x-axis that connects the central C-atom of the PTM unit to the Fe-atom of the Fc unit. The top panel shows the F-dependence of μ_x, the x-component of the molecular dipole moment, which is given by

$$\mu_x = e \sum_p q_p x_p \qquad (7)$$

where e is the electronic charge, x_p is the x-coordinate of the p-atom, and q_p is the Coulson net atomic charge, defined as[19,21]

$$q_p = Z_p - \sum_{\lambda \in p} P_{\lambda\lambda} \qquad (8)$$

In this expression Z_p is the charge of pth atomic core, λ runs on all atomic orbitals centered on p, and $P_{\lambda\lambda}$ is electronic density matrix,

$$P_{\lambda\lambda} = \sum_i n_i |c_{\lambda i}|^2 \qquad (9)$$

where i runs on the molecular orbitals with n_i electrons and $|c_{\lambda i}|^2$ is the weight of the λth atomic orbital in the ith MO.

The S-shaped $\mu_x(F)$ curve in Figure 4 clearly points to two different regimes: a low and a high field regime separated by a region at $F \approx 0.4$ V/Å where charges rearrange dramatically. In the central panel the linear polarizability, $\alpha \propto \partial \mu_x/\partial F$, shows a large peak at the interface that separates two regions of almost constant polarizability, marked by the blue and red shadows in the figure. These two regions correspond to two different regimes for Fc-PTM: an almost neutral regime with the ground-state largely dominated by the $DA^{\bullet}$ state and a zwitterionic regime, dominated by the $D^{+\bullet}A^{-}$ state. To further support this interpretation, the bottom panel of Figure 4 shows the total charges on the PTM and Fc units. The sum of the charges on the two units is approximately zero, confirming the picture of a charge transfer from D to A. Moreover, in the small F regime the charge transferred from D to A is of the order of 0, while

(18) (a) Tsiper, E. V.; Soos, Z. G. *Phys. Rev. B* **2001**, *64*, 195124. (b) Soos, Z. G.; Tsiper, E. V.; Pascal, R. A., Jr. *Chem. Phys. Lett.* **2001**, *342*, 652. (c) Tsiper, E. V.; Soos, Z. G.; Gao, W.; Kahn, A. *Chem. Phys. Lett.* **2002**, *360*, 47. (d) Tsiper, E. V.; Soos, Z. G. *Phys. Rev. B* **2003**, *68*, 085301. (e) Soos, Z. G.; Tsiper, E. V.; Painelli, A. *J. Lumin.* **2004**, *110*, 332.

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

(20) Owing to disorder two slightly different molecular conformations are found (see ref 7). Here we discuss results obtained for the dominant configuration. Qualitatively similar results are obtained for the other configuration, with about 20% larger M values.

(21) See e.g.: *Chemoinformatics: A Textbook;* Gasteiger, J., Engel, T., Eds.; Wiley: Darmstadt, Germany, 2007.
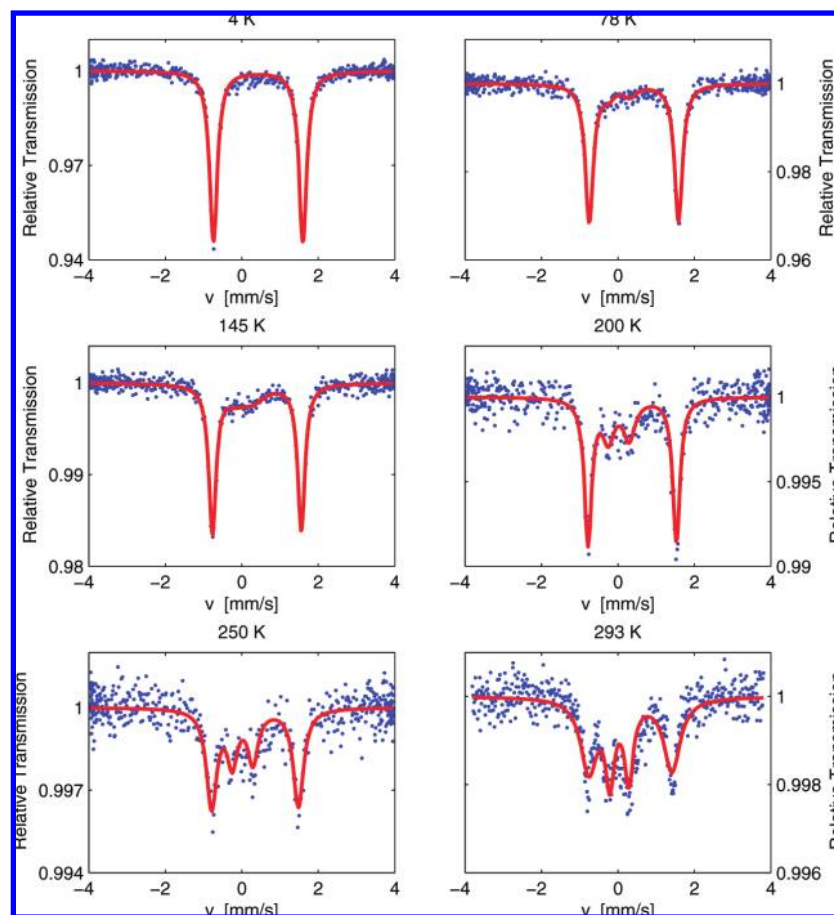
Figure 5. Temperature dependence of Mossbauer spectra of Fc-PTM. Dots are experimental data extracted from ref 8. Red lines are fittings of experimental data based on the proposed model for bistability (see text and Supporting Information for fit parameters).

the region of the second plateau corresponds to a system where approximately one electron is transferred. A reasonable estimate for the charge distribution in the zwitterionic form of Fc-PTM can then be obtained from the charge-distribution calculated for an Fc-PTM molecule in an electric field $0.65 < F < 0.9$ V/Å, corresponding to the red-shadowed region in Figure 4.

We can now estimate M on the basis of the molecular charge distribution described by the Coulson net atomic charges calculated for the Fc-PTM molecule in the zwitterionic regime. To ensure at least two significant digits in the estimate of M, we sum all interactions among ~19000 molecular sites (17 × 17 × 33 unit cells). For F values corresponding to the zwitterionic regime (the red region in Figure 4) we estimate M ranging between −1.0 (for $F = 0.65$ V/Å) to −1.5 eV (for $F = 0.9$ V/Å). For comparison, in the neutral regime (blue area in the same figure) $|M| < 0.05$ eV confirming that electrostatic interactions between neutral molecules are indeed negligible.

This estimate of M safely locates Fc-PTM crystals in the bistability region and is consistent with bistable behavior for Fc-PTM suggested by Mössbauer spectra collected for Fc-PTM crystals at different temperatures in ref 8, and reported in Figure 5. In the 4.2 K spectrum only the doublet assigned to the neutral ferrocene species appears,[8] indicating that the neutral DA• form of Fc-PTM largely dominates at low temperature. With increasing temperature, an additional doublet appears in Mössbauer spectra, characteristic of the ferrocinium ion, showing the appearance of the zwitterionic D+•A− form of Fc-PTM.[8] The intensity of the ferrocinium doublet increases with temperature

at the expense of the intensity of the ferrocene doublet, suggesting an increasing population of Fc+•PTM−. At 293 K the relative intensity of the two signals is comparable, pointing to similar population of the two species. To rationalize this behavior a model is required for the temperature-dependence of the relative Fe(III)/Fe(II) population. In line with the mean-field approximation adopted above, and in close analogy with textbook treatments of ferromagnetism,[22] we describe the crystal as a collection of noninteracting molecules that can only occupy the two stable N and I states, separated by an energy gap ΔE, as shown in Figure 3d,e. The relative population of the two species is governed by the Boltzmann equation. While coherent with the mean-field approximation, this procedure does not account for any phenomenon related to the finite size of the coexisting N and I domains, and in particular disregards the energy of domain boundaries. Moreover M in eq 3 depends on interatomic distances and, as such, it is a temperature-dependent parameter. In the lack of temperature-dependent crystallographic data, and in view of the approximate nature of the model adopted for the population statistics, we disregard the temperature dependence of M.

With these approximations, the six experimental Mössbauer spectra in Figure 5 are fitted as a sum of two couples of Lorentzian bands (corresponding to the Fe(II) and Fe(III) doublets) with adjustable positions and widths at each temperature (see Supporting Information for actual values) while

(22) See e.g.: *Introduction to Modern Statistical Mechanics*, Chandler, D., Ed.; Oxford University Press: New York, 1987; Chapter 5.

keeping fixed the ΔE parameter that governs the temperature-dependence of the Fe(III)/Fe(II) population ratio. The best fit to experimental data was obtained for $\Delta E \approx 0.014$ eV corresponding to a molar Fe(III) fraction ranging from 0 to 36% as temperature increases from 4.2 to 293 K. In view of the many approximations involved in the model, the overall quality of the fit is good, as it can be appreciated from data in Figure 5. More quantitatively, referring to the reduced $\tilde{\chi}^2 = \chi^2/p$ (where p is the number of degrees of freedom) as the standard indicator for the quality of the fit,[23] we estimate $\tilde{\chi}^2 \approx 1.11$, similar to the value extracted from the original fit ($\tilde{\chi}^2 \approx 1.07$) where, however, the Fe(III)/Fe(II) population ratio is taken as a free adjustable parameter for each T (leading to an increase of 5 units in the total number of free parameters). The largest difference between our results and the analysis carried out in ref 8 is found for the room temperature spectrum (cf Supporting Information) where our constrained fit suggests a molar fraction of Fe(III) $\approx 36\%$, to be compared with the previous estimate amounting to 63%. However, the deconvolution of the partly overlapping four Lorentzian bands in the 293 K spectrum in Figure 5 is hindered by the poor signal-to-noise ratio at this temperature.

Our analysis of Mössbauer spectra in Figure 5 is consistent with the proposed model for Fc-PTM. In fact the estimated $\Delta E \approx 0.014$ eV corresponds to the value obtained for Fc-PTM molecular parameters, fixing $M = -1.1$ eV (corresponding to an effective $M - \varepsilon_v = -1.2$ eV, cf. Figure 3d), well in line with the results from quantum chemical calculations, $-1.5 < M < -1.0$ eV.

IV. Discussion and Conclusions

The cooperative nature of electrostatic interactions in molecular materials with low-lying charge-transfer degrees of freedom is responsible for new and interesting physics whose most dramatic manifestation is the appearance of discontinuous phase transitions and of the related phenomena of multistability.[5,6] McConnell first recognized the important role of intermolecular interactions in mixed stack charge-transfer salts,[24] an interesting family of molecular materials that shares some basic physics with crystals of DA chromophores.[5,6] In charge-transfer salts planar electron-donor and acceptor molecules (typical examples being tetrathiafulvalene, TTF, and chloranil, CA, respectively) pack in one-dimensional arrays (stacks) with an alternating (mixed)...DADA... motif.[25] Electrons can hop back and forth from each D molecule toward the two nearest A molecules, leading to a system with truly delocalized electrons in one-dimension. The seminal work by McConnell triggered research in the field of charge-transfer crystals, leading to the discovery of the neutral-ionic phase transition in TTF-CA.[26] Quite impressively, the phenomenon of phase coexistence was also suggested in the same work.[24] This early model for charge-transfer crystals disregarded the hybridization energy: a too

crude approximation, as it was recognized early.[16,25,27] More refined models have been progressively developed,[28] supported by an increasing set of experimental data,[28] and recently one of us has discussed the coexistence of phases observed at the pressure-induced neutral to ionic phase transition of TTF-CA in terms of bistability induced by electrostatic intermolecular interactions.[29]

Crystals of (closed or open-shell) DA molecules differ from charge-transfer crystals because in the latter electrons are truly delocalized in one dimension. The strict confinement of electrons within each molecular unit in crystals of DA chromophores greatly simplifies the description of the system without spoiling the cooperative nature of electrostatic intermolecular interactions.[5,6] The possible appearance of discontinuous charge crossovers and bistability in crystals of DA chromophores has been proposed a few years ago,[5] but so far this suggestion has not found experimental demonstration. Here, a detailed analysis of optical spectra of Fc-PTM in solution, and the modeling of electrostatic interactions in the crystalline phase, supported by quantum chemical calculations, suggest that the coexistence of neutral and zwitterionic Fc-PTM species inferred by temperature-dependent on Mössbauer spectra of Fc-PTM crystals can be quantitatively understood in terms of electrostatically induced bistability.

We take advantage of the molecular nature of Fc-PTM crystals in a bottom-up modeling strategy.[5,12] In brief, this strategy consists in the analysis of absorption spectra of Fc-PTM in solution, based on an essential two-state model,[11] to extract a set of environment-independent molecular parameters. These parameters are then transferred to a model Fc-PTM molecule in the crystals. The two-state model suffers of obvious limitations, but it proved useful and reliable in the description of optical spectra of several closed-shell DA chromophores.[11] The model for electrostatic intermolecular interactions is based on the description of the charge distribution on each molecule in terms of point atomic charges,[18] obtained from quantum chemical calculations.[19] The delicate issue in this context is the need to evaluate the charge distribution on zwitterionic molecules, while gas-phase (or solution) calculations invariably lead to (almost) neutral molecules. To overcome this problem we performed calculations on a molecule in an applied static electric field, as to force it to the zwitterionic state. Of course a uniform electric field hardly mimics the nonhomogeneous electrostatic potential in the crystal:[18] the electric field introduced in quantum chemical calculations must be considered just as a numerical device to force the molecule in the zwitterionic form.

In conclusion, the coexistence in a crystalline sample of both the neutral and zwitterionic forms of Fc-PTM, as shown by Mössbauer spectra,[8] is a result of the bistability of Fc-PTM crystals induced by electrostatic intermolecular interactions. On general grounds, bistability can show up either with hysteresis loops or phase coexistence, depending on experimental conditions.[4] As originally recognized by McConnell,[24] coexistence is most probably observed in systems like Fc-PTM, where the weak electron-vibration coupling implies similar geometries for the two stable forms, and hence minor strain contributions to the boundary energies. Bistability is a rare and interesting phenomenon, induced in crystals of valence tautomeric DA molecules by *cooperative* intermolecular electrostatic interac-

(23) See e.g.: *Numerical Recipes*; Press, W. H., Flannery, B. P., Teukolsky, S. A., Vetterling, W. T., Eds.; Cambridge University Press: New York, 1986; Chapter 14.

(24) McConnell, H. M.; Hoffman, B. M.; Metzger, R. M. *Proc. Natl. Acad. Sci. U.S.A.* **1965**, *53*, 46.

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(28) See e.g.: Girlando, A.; Painelli, A.; Bewick, S. A.; Soos, Z. G. *Synth. Met.* **2004**, *141*, 129.

tions coupled to intramolecular charge-transfer. Bistability is expected in crystals of largely neutral (closed- or open-shell) DA molecules with attractive electrostatic intermolecular interactions. To support bistability the valence tautomeric DA molecule must be characterized by a small positive τ/z ratio. Reliable estimates of z and τ can be obtained from the analysis of optical spectra of the molecule in solution: DA molecules with small τ/z typically show the intervalence absorption band down in the red or infrared spectral regions, with normal solvatochromic behavior. The $z \sim -M/2$ constraint implies a delicate balance between molecular and intermolecular energies. Following a similar strategy, as successfully adopted in the quest for the neutral−ionic phase transition in CT salts,[26] we suggest a systematic study of families of crystals of DA molecules with tunable D and A sites as to systematically vary z.

Supporting Information Available: Absolute energy of Fc-PTM molecule obtained from PM6 calculations and the corresponding Cartesian coordinates. Fit parameters for Mössbauer spectra in Figure 5 and the comparison of resulting Fe(III) fractions with results from ref 8. This material is available free of charge via the Internet at http://pubs.acs.org.

JA803049G

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