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Introduction

The fundamental paradigm in the fabrication of molecular materials is the transition from molecules to materials. Tailoring the materials' responses and attributes is generally achieved by tuning the structure and functionalities of the molecular building blocks and through them their assemblies, an approach that could be termed as intrinsic design. The contrasting scenario would be the control of molecular assembly mediated by extrinsic factors such as template or substrate effects,^{1,2} electric/magnetic fields^{3,4} and mechanical constraints.5 Organized assembly of molecules into crystalline lattices makes the elucidation of the materials' structureproperty correlations and further design optimization especially convenient. However an important aspect that warrants consideration is the feasibility of realizing a hierarchical assembly of molecules from the isolated (or solvated) state through an amorphous solid form to the final crystalline state, and its potential implications for the materials' attributes. The amorphous state opens up a new dimension in the moleculesto-materials transition and offers the opportunity to fine-tune

Hierarchical assembly of a molecular material through the amorphous phase and the evolution of its fluorescence emission[†]

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Fabrication of an amorphous phase followed by a hierarchy of forms leading to the crystalline state offers a new dimension in the assembly of small molecule based materials. The morphology and extent of crystallinity of the nanostructures in drop-cast thin films of a diaminodicyanoquinodimethane molecule are shown to be tunable through the variation in the composition of the solvent mixture used for dropcasting. The different states of assembly starting from the solvated molecule through amorphous spherical particles, crystalline nanofibers and nano/microcrystals to bulk crystals are shown to be accompanied by a smooth variation of the fluorescence emission, the color evolving from green to blue, and the efficiency increasing steadily with the overall enhancement from the solution to the bulk crystalline state being ~400 times. Quantum chemical computations on the molecule and its H-bonded dimer and π -dimers provide insight into the impact of intermolecular interactions in the crystalline assemblies on the electronic structure. The current study illustrates a significant departure from the conventional molecules-to-materials transition, opening up new hierarchical pathways of assembly of molecular materials.

> the properties of the molecular assembly. It is notable that the reversible transition between the amorphous and crystalline states is the basis of commercially important phase-change materials based on inorganic systems.6 The amorphous state of molecular nanomaterials is also relevant in the context of the two-step nucleation theory of fundamental interest in crystal growth.7-9

> The coexistence of amorphous and crystalline regions in polymers and their critical role in determining the materials' properties are well recognized; the extent of crystallinity is a basic characteristic of any polymeric material. A recent example of interest for light emitting materials is the tuning of the crystallinity of poly(3-hexylthiophene) nanoparticles by varying the solvent composition.10 In the domain of small molecule based materials, the amorphous phase and its attributes have been less widely realized and exploited. One of the few cases relates to electroluminescent systems and charge mobilities promoted by the amorphous nature.11 Thermal and solvent vapor induced amorphous-to-crystalline transformation (ACT) has been explored in thin films^{12,13} and dye aggregates.14,15 We have developed a simple protocol for the ACT of nanoparticles of a diaminodicyanoquinodimethane (DADQ) derivative accompanied by fluorescence switching and enhancement.¹⁶ The process involves fixing the nanoparticles (obtained by drop-casting dilute solutions on glass substrates) in a polymer thin film and solvent vapor fuming inducing the ACT of the partially confined particles. We have also investigated the utility of mechanical control of the aggregation of an

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amphiphilic DADQ molecule at the air-water interface and its impact on the optical responses of the resulting monolayer Langmuir-Blodgett films.¹⁷

Aggregation induced enhancement of fluorescence,18,19 as opposed to its quenching, is of considerable interest from the perspectives of both molecular level interactions/assembly as well as applications such as displays and sensors. Enhancement of the fluorescence of DADQ molecules from their solution to the crystalline solid state has been investigated in detail in our laboratory.20 The size-dependent optical responses of nano/ microcrystals²¹ and the enhancement of fluorescence in the solution and colloidal states of a DADQ derivative by polyelectrolyte templating have also been explored.22 Since the fluorescence emission wavelength and efficiency of DADQs are strongly sensitive to the molecular environment as well as the rigidification of their structures, it would be interesting to explore the hierarchical assembly of these molecules through the amorphous state and monitor the consequence to the fluorescence characteristics.

Introduction of aromatic groups through conformationally labile bonds onto the DADQ framework promotes the formation of amorphous particles in thin films formed by drop-casting their dilute solutions on glass substrates.16 In the present study we have synthesized and structurally characterized a new DADQ molecule, 7-pyrrolidino-7-benzylamino-8,8-dicyanoquinodimethane (PBEDQ). Drop-cast thin films obtained from solutions of PBEDQ with varying compositions of a good solvent and a nonsolvent revealed nanostructures ranging from amorphous spherical particles, to crystalline fibers, to faceted nano/microcrystals, and intermediate composite structures. A parallel evolution of the fluorescence emission in terms of color as well as intensity is observed. The study demonstrates the utility of extending the hierarchical stages of molecular assembly by introducing the new dimension of the amorphous state, and its significant consequences for the materials' responses.

Experimental and computational

Synthesis

PBEDQ was synthesized in two steps starting from 7,7,8,8-tetracyanoquinodimethane (TCNQ) (Scheme 1). Pyrrolidine was reacted with TCNQ in \sim 1 : 1 mol ratio to yield 7-pyrrolidino-7,8,8-tricyanoquinodimethane (PTCNQ) which on reacting with benzylamine yielded PBEDQ.²³

Crystal structure

Crystals were grown by slow evaporation of an acetonitrile solution. A single crystal X-ray diffraction study was carried out at 100 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo K_{α} finefocus sealed tube ($\lambda = 0.71073$ Å) operated at 1200 W power (40 kV, 30 mA). The detector was placed at a distance of 6.003 cm from the crystal. A total of 2400 frames were collected with a scan width of 0.3° in ω mode and an exposure time of 5 s per frame. The frames were integrated with the Bruker SAINT software using a narrow-frame integration algorithm. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multi-scan method (SADABS). The structure was solved and refined using the Bruker SHELXTL (Version 6.14) Software.²³ X-ray diffraction data of powder samples were recorded on a SMART Bruker D8 Advance X-ray diffractometer using Cu K_{α} radiation $(\lambda = 1.5406 \text{ Å})$ at 40 kV and 30 mA.

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Spectroscopy

Electronic absorption spectra were recorded on a Varian Model Cary 100 UV-vis spectrometer. Solid samples were prepared by rubbing small amounts of the microcrystalline powder onto quartz plates; the quantity was varied to achieve the desired optical density at the excitation wavelength. Drop cast films on glass/quartz were also studied. Diffuse reflectance spectra of the samples were recorded using the DRA-CA-30I accessory and converted to absorption spectra using the Kubelka-Munk function. Steady-state fluorescence excitation and emission spectra were recorded on a Horiba Jobin Yvon Model FL3-22 Fluorolog spectrofluorimeter. The spectra were recorded in right angle geometry with the samples mounted on a solid sample holder. The optical density of the samples was maintained below 0.3 to avoid inner-filter effects. The fluorescence quantum yield of the solution was estimated by comparison with quinine sulfate in 1 N H₂SO₄ ($\phi = 0.546$).²⁴ The absolute value of the fluorescence quantum yield of solid samples was determined using an integrating sphere and the PLQY Calculator v.3 software.

Microscopy

A Carl Zeiss model Ultra 55 FESEM and Philips Model XL30 SEM were used to observe directly the morphology of the nanostructures in the drop-cast thin films prepared on the glass substrate; the samples were coated by a thin layer of sputtered gold and 20 kV beam voltage was used. An FEI model TECNAI G² 20 S-Twin TEM operated at 200 kV was used to image the nanostructures and record the electron diffraction; the sample preparation procedure is discussed later. A Carl Zeiss LSM 710 NLO ConfoCor 3 laser scanning confocal microscope was used to record the fluorescence images of the drop-cast films on glass/quartz; $\lambda_{exc} = 365$ nm, $\lambda_{em} = 417$ -600 nm. Fluorescence lifetimes in solution drops and drop-cast films were probed using the time-domain technique with a MicroTime 200 Instrument (PicoQuant) coupled to an Olympus IX71 Microscope (PicoQuant). Excitation was achieved using a 405 nm



Scheme 1

pulsed laser diode and the fluorescence observed through a 430 nm long pass filter. The FWHM of the pulse response function was 176 ps. The intensity decays were analyzed with a multi-exponential model using SymPhoTime v. 5.0 software.²³

Computations

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Ab initio quantum chemical computations were carried out using the density functional method at the B3LYP/6-31G* level; the Gaussian03 program was used.25 Geometry optimization was carried out for the isolated molecule as well as for the molecule with different solvent environments using the selfconsistent reaction field (SCRF) approach. The solvation model provides a useful approximation of the microscopic environment of the molecule in the crystal lattice;²⁶ the appropriate solvent was chosen based on the agreement of the computed structure with that observed in the crystal, specifically in terms of the characteristic dihedral twist angle of the DADQ framework that is sensitive to the dielectric environment. Electronic excitation profiles of the molecule and its H-bonded dimer and π -dimers extracted from the crystal lattice were calculated using the time-dependent density functional (TD-DFT) method; the impact of the lattice environment was incorporated using the solvation model.

Results and discussion

Crystals of PBEDQ grown from acetonitrile solution are found to belong to the $P2_1/n$ space group with one molecule in the asymmetric unit. The molecular structure (with one of the disordered carbon atoms²³ placed in the average position) and the unit cell packing are shown in Fig. 1; the significant crystallographic data are collected in Table 1. The molecular structure shows the prominent twist between the diaminomethylene moiety and the benzenoid ring plane (bearing the dicyanomethylene group) characteristic of DADQ molecules;^{26,27} the relevant dihedral angles are $\tau_{N9-C7-C1-C2} = 54.7^{\circ}$, and $\tau_{N10-C7-C1-C6} = 58.3^{\circ}$. Intermolecular H-bonds between the amine H and one of the cyano Ns $[r_{H10\cdots N13'} = 2.001$ Å, $\theta_{N10-H10\cdots N13'} = 160.2^{\circ}]$ lead to extended supramolecular chains along the $[1 \ 0 \ \overline{1}]$ direction. The benzenoid rings show a slipped

Fig. 1 (a) Molecular and (b) crystal structures of PBEDQ from X-ray diffraction analysis. C (grey), N (blue), and H (white) atoms are indicated, and the disordered C17 is shown at the averaged position and the H atoms (except the amine ones) are omitted in (b) for clarity.

 Table 1
 Crystallographic data for PBEDQ

Empirical formula	$C_{21}H_{20}N_4$
Crystal system	Monoclinic
Space group	$P2_1/n$
$a/ m \AA$	9.4123 (7)
b/Å	12.9289 (10)
c/Å	14.5929 (11)
β/deg.	99.2920 (10)
$V/Å^3$	1752.5 (2)
Ζ	4
$ ho_{ m calc.}/ m g~cm^{-3}$	1.245
μ/cm^{-1}	0.76
Temperature/K	100 (2)
λ/Å	0.71073
No. of reflections	3087
No. of parameters	240
Max., min. transmission	0.976, 0.967
GOF	1.060
$R [\text{for } I \ge 2\sigma_{\text{I}}]$	0.0416
wR^2	0.1090
Largest difference peak and hole/e \mathring{A}^{-3}	0.376/-0.309

 π - π contact with an interplanar distance of 2.772 Å and a centroid-centroid distance of 5.121 Å; these contacts link the H-bonded chains into sheet structures in the *ac* plane (Fig. 2). Another intermolecular slipped π - π contact between the phenyl rings of the benzylamine group is also observed in the crystal structure.²³

Electronic absorption and fluorescence emission spectra of PBEDQ in acetonitrile solution and as a microcrystalline solid are presented in Fig. 3. The solution shows an absorption with λ_{max} at 370 nm. This arises due to the intramolecular charge transfer, a characteristic feature of the zwitterionic benzenoid framework of DADQ molecules.^{20,28} The solid shows a broad (320–400 nm) absorption in the same region. The fluorescence emission shows λ_{max} at 512 and 456 nm in the solution and solid respectively. The significant blue shift of the peak in the solid is accompanied by an enhancement of intensity of ~400. Quantum chemical computations were carried out to gain insight into these spectral shifts. The solution absorption was computed using the fully optimized structure of PBEDQ; the

Fig. 2 H-bonding (cyan broken line) and short intermolecular contacts (pink broken line) involved in the π - π interaction leading to layer structures in crystals of PBEDQ. C (grey), N (blue), and H (white) atoms are indicated, the disordered C17 is shown at the averaged position and the H atoms (except those involved in H-bonding) are omitted for clarity.

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Fig. 3 (a) Optical absorption spectra (with concentrations adjusted to match peak absorbances) and (b) normalized fluorescence emission spectra of acetonitrile solution and microcrystalline solid of PBEDQ (inset: relative emission intensity of samples with matched optical density).

molecular structure from the crystal was used as the starting point for the optimization and the acetonitrile solvent environment was included in the computation. The significant absorption λ_{max} (with high oscillator strength) is found at ~386 nm (Table 2), in good agreement with the solution spectrum. The dihedral twist angle in the optimized molecular

Table 3 Spectroscopic features of PBEDQ dimers from the crystal obtained from the B3LYP/6-31G* and B3LYP/6-31G*/SCRF computations (see the ESI for the structures). The absorption with $\lambda_{max} > 250$ nm and the oscillator strength (f) > 0.1 are listed. The specific data directly relevant to the discussion in the text are shown in italics

	λ_{\max} (nm) [f]		
Structure	Vacuum	Water	
H-bonded dimer	480.8 [0.40]	364.3 [0.52]	
	470.9 0.25	359.6 [0.46]	
	292.4 0.30	260.1 [0.26]	
	291.0 0.26	259.6 0.21	
π-dimer 1	414.0 0.55	354.2 [0.76]	
	277.8 [0.48]	264.1 [0.17]	
		257.3 [0.25]	
π-dimer 2	495.8 [0.63]	366.4 [0.93]	
	300.7 [0.75]	264.0 [0.38]	
		260.7 [0.10]	

structure of DADQs is sensitive to the dielectric constant of the environment imposed during the optimization.²⁶ In the case of PBEDQ, an environment equivalent to that of water is required to reproduce the dihedral twist of the molecule in the crystal (Table 2). This indicates that within this simple model, the dielectric environment of the molecule in the crystal can be mimicked using water solvation. The absorption features computed for the PBEDQ monomer and different dimers are collected in Tables 2 and 3 respectively. From the computations including water solvation, it is seen that the λ_{max} (with high oscillator strength) decreases down to \sim 354 nm. These results indicate that the molecular packing in the crystal lattice and the electronic interaction between the chromophores lead to the blue shift in the optical absorption. This is likely to be the cause for the blue shift in the emission peak as well. The fluorescence enhancement in the solid state can be attributed to the prevention of excited state geometry relaxation which, in the solution state, leads to non-radiative decay.20,22

In a conventional reprecipitation process, injection of small amounts of an acetonitrile solution of PBEDQ into toluene (nonsolvent for PBEDQ) produced a colloid. The colloid shows a blue emission characteristic of crystalline PBEDQ. It was filtered

Table 2 Geometric and spectroscopic features of the PBEDQ molecule from the B3LYP/6-31G* and B3LYP/6-31G*/SCRF computations (see the ESI for the structures). The two dihedral angles (see the text for details) and the average value for each structure are shown and the absorption with $\lambda_{max} > 250$ nm and oscillator strength (f) > 0.1 are listed. The specific data directly relevant to the discussion in the text are shown in italics

Molecular geometry	Twist angles, τ [average] (deg.)	$\lambda_{\max} (nm) [f]$		
		Vacuum	Acetonitrile	Water
From crystal structure	58.3, 54.7 [56.5]	512.4 [0.33]	372.7 [0.47]	367.6 [0.48]
		303.4 0.37	264.1 0.27	262.4 [0.26]
Optimized (vacuum)	33.6, 36.4 [35.0]	430.0 [0.80]		
		272.2 0.11		
Optimized (acetonitrile)	53.4, 53.6 [53.5]		386.0 [0.56]	_
			262.3 [0.23]	
Optimized (water)	55.1, 54.8 [55.0]	_		378.3 [0.54]
				262.4 0.23

through a nanoporous membrane and observed in an FESEM; the formation of fibrous nanostructures could be discerned clearly.²³ The spectroscopy and microscopy observations suggest that PBEDQ molecules assemble into crystalline fibers in the presence of toluene. This prompted us to explore, in detail, thin films of PBEDQ fabricated by drop-casting solutions with different acetonitrile–toluene compositions.

Typically 0.3-0.6 mM solutions of PBEDQ in acetonitriletoluene mixtures with varying compositions (100:0 to 10:90 v/v) were drop-cast on glass/quartz substrates and the resulting films dried quickly in ambient atmosphere. FESEM images illustrating the morphology of the thin films formed are collected in Fig. 4. The shape of the particles is spherical in the case of pure acetonitrile. The morphology is characteristic of amorphous nanoparticles formed by DADO derivatives possessing aromatic substituent groups connected through conformationally labile bonds.¹⁶ With the introduction of small amounts of toluene in the solvent, the drop-cast films show spherical particles together with fibrous nanostructures. The presence of toluene not only reduces the solubility of PBEDO, but also slows down the drying of the drop-cast film. When the toluene content is increased, the nanofibers become the dominant structures, and the film is exclusively made of the fibers when the acetonitrile-toluene composition is 40 : 60. It may be noted that crystalline organic fibers have been fabricated earlier by the fast evaporation of capillary films.²⁹ The emergence of faceted nano/microcrystals of PBEDQ is observed when the solvent composition reaches 10:90. By coating the drop-cast films with a thin layer of polystyrene, drying and peeling off, we have fabricated free-standing films containing the nanostructures fixed in it. Placing these on a

carbon-coated copper grid and dissolving the polystyrene film in toluene, TEM images of the nanostructures could be recorded. Images of the structures formed in the drop-cast films obtained using the 100:0, 40:60 and 10:90 acetonitrile-toluene mixtures are shown in Fig. 5; the morphologies are similar to those in the FESEM images (Fig. 4). The spherical particles obtained in the first case (Fig. 5a) gave no electron diffraction pattern; this observation is consistent with its amorphous nature. The nanofibers (Fig. 5b) produced a welldefined ring pattern typical of polycrystalline materials; the lattice spacing is consistent with one of the reflections in the PBEDQ crystal, indicating a preferred growth direction.²³ The nanocrystals (Fig. 5c) gave clear electron diffraction spots which could also be indexed to the lattice structure of PBEDO.²³ In a separate experiment, we have enriched the content in the acetonitrile-toluene solution (10:90) by keeping it for several hours and filtered through a nanoporous membrane. The powder X-ray diffraction pattern of the particles obtained²³ is fully consistent with the crystal structure of PBEDO, confirming the crystalline nature and ruling out the formation of any polymorphic structures.

Absorption and emission spectra of the drop-cast films are collected in Fig. 6a and b respectively. The relatively broad absorption spectrum with higher baseline of the film with the spherical particles can be attributed to stronger scattering from the amorphous particles; the impact of different environments of the chromophores cannot be ruled out. The emission spectra are recorded by exciting at the maximum of the fluorescence excitation spectrum in each case;²³ they reveal the evolution from amorphous to crystalline nanostructures, consistent with the microscopy observations above. The film with spherical particles obtained from the acetonitrile solution shows



Fig. 4 FESEM images of thin films fabricated by drop-casting PBEDQ in acetonitrile-toluene mixtures with varying compositions: (a) 100 : 0, (b) 80 : 20, (c) 40 : 60, (d) and (e) 10 : 90. Scale bar is 1 μ m in (a) to (d) and 5 μ m in (e).

Fig. 5 TEM images (along with the SAED) of nanoparticles, nanofibers and nano/microcrystals fabricated by drop-casting PBEDQ in acetonitrile-toluene mixtures with the compositions: (a) 100 : 0, (b) 40 : 60 and (c) 10 : 90.



Fig. 6 (a) Absorption and (b) emission spectra of thin films fabricated by drop-casting (on quartz) PBEDQ in acetonitrile–toluene mixtures with varying compositions. (c) CIE chromaticity plot of the thin films fabricated by drop-casting acetonitrile–toluene mixtures of different compositions [100 : 0 (spherical particles); 80 : 20 (spherical particles + fibers); 40 : 60 (fibers); 10 : 90 (fibers + nano/microcrystals)] together with those of the solution and microcrystalline solid.

emission ($\lambda_{max} \sim 488$ nm) close to green, reminiscent of the solution. With increasing toluene content in the solvent used for drop-casting, the peak shifts steadily to the blue; emission of the films with nanofibers and nano/microcrystals resemble that of the bulk microcrystalline solid ($\lambda_{max} \sim 460$ nm). The emission spectrum of the films containing both spherical particles and fibers is slightly sensitive to the excitation wavelength, as it depends on the relative content of the two morphologies.²³ Tuning of the emission across the series of drop-cast thin films can be visualized by the confocal fluorescence images taking into account also the spectral responses from the individual nanostructures (Fig. 7). Fine-tuning of the emission color across the series (including also the solution and bulk solid) is clearly demonstrated by the chromaticity plot in Fig. 6c. Significantly, the quantum yield for the emission is also found to increase across the series (Table 4), in parallel to the extent of crystallinity. This is consistent with the general concept of lattice rigidification inhibiting structural (rotational) relaxation of the excited state of DADQ molecules leading to fluorescence enhancement.20,22 FLIM images of the drop-cast films23 illustrate the progression of excited state lifetimes across the series (Table 4) consistent with the fluorescence emission enhancement.

Subtle variations in the drop-casting conditions and treatment of the drop-cast films lead to the formation of a wide range of morphologies with varying amorphous/crystalline structures. The following typical examples illustrate this. Enclosing the films drop-cast from an acetonitrile solution (3 mM) inside a covered Petri dish slows down the evaporation of the solvent and drying of the film, leading to the formation of nanofibers (Fig. 8a) instead of the spherical particles. Films obtained by quick drying, made up of the spherical particles (Fig. 4a), when exposed again to acetonitrile vapors show the formation of nanofibers emanating from the spherical seeds (Fig. 8b), a vivid illustration of the crystalline structures emerging smoothly from the amorphous ones. Slow evaporation of the solvent in the films drop-cast from methanol solutions of PBEDQ reveal spherical particles enveloped in a fiber network (Fig. 8c). These observations point to the rich variety of morphologies and more significantly, extents of crystallinity of the PBEDQ nanostructures that can be realized by optimization of the conditions for fabrication of the drop-cast thin films. An earlier study of some interest in this context is the control of self-assembly and long-range orientational order in H-bonded oligothiophene polymorphs through variation of solvent evaporation and crystal growth conditions.30





Fig. 7 Confocal fluorescence images of thin films fabricated by drop-casting PBEDQ in acetonitrile–toluene mixtures with varying compositions: (a) 100 : 0, (b) 80 : 20, (c) 40 : 60, (d) 10 : 90. Scale bar = 5 μ m; false colors are used in the images based on the spectral response of the full sample.²³ (e) Confocal fluorescence spectral responses from the individual nanostructures in (b).

 Table 4
 Fluorescence quantum yield and average excited state lifetime of PBEDQ in different states, solution to drop cast films of varying amorphous/ crystalline nature to microcrystalline solid

Acetonitrile– toluene	Structure	Quantum yield (%)	Average life time (ns)
_	Solution	0.1	<0.18
100:0	Film	1.6	0.64
	(spherical particles)		
80:20	Film	2.2	0.89
	(spherical particles +		
	fibers)		
40:60	Film (fibers)	4.4	1.02
10:90	Film	6.5	1.93
	(fibers + nano/		
	microcrystals)		
_	Microcrystalline solid	36.4	2.63



Fig. 8 FESEM images of thin films fabricated by drop-casting PBEDQ in (a) acetonitrile and evaporating the solvent slowly, (b) acetonitrile, evaporating the solvent quickly and then exposing to acetonitrile vapors, and (c) methanol and evaporating the solvent slowly. Scale bar = $1 \mu m$.

Tuning of the crystallinity and optical responses of PBEDQ nanostructures has interesting parallels and significant contrasts with the case of conjugated polymer nanoparticles of poly(3-hexylthiophene) mentioned in the Introduction.¹⁰ In both cases, the extent of crystallinity is controlled by the solvent composition, and the increasing content of the nonsolvent enhances the crystallinity. The present study is a novel illustration of such phenomena with small molecule based materials. While the extent of crystalline assembly primarily influences the electronic absorption features and photoluminescence decays in the polymer nanoparticles, the case of PBEDQ involves prominent changes in the emission characteristics in terms of the color and more significantly the quantum yields, aspects of considerable interest in practical applications.

Conclusions

A new diaminodicyanoquinodimethane derivative PBEDQ is synthesized, structurally characterized and demonstrated to be an interesting system to develop strongly fluorescent nanostructures. The nanostructures of PBEDQ in thin films fabricated by drop-casting solvent mixtures of varying compositions exhibit a smooth progression of morphologies and crystallinity. While the solution and the crystalline solid state represent the two extremes of molecular materials commonly studied, the nanostructures of PBEDQ including the amorphous phase represent logical intermediates in the course of supramolecular assembly and the evolution of fluorescence characteristics in terms of energies and efficiencies. The current explorations establish a fundamentally interesting approach to new luminescent molecular materials based on tuned assembly.

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