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Supramolecular helical self-assemblies and large stokes shift in 1-(2-cyanophenyl)piperazine and 4-piperidinopiperidine bis-substituted tetracyanoquinodimethane fluorophores

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ABSTRACT

Heterocyclic building blocks such as 1-(2-cyanophenyl)piperazine (1,2-CPP) and 4-piperidinopiperidine (4-PP) are very well known in oncological medicines like platins and camptothecins. Utilization of 1,2-CPP and 4-PP in the reaction with tetracyanoquinodimethane (TCNQ) produced two latest compounds, bis (1,2-cyanophenylpiperizino)dicyanoquinodimethane (1,2-CPPDQ) [**1**] and bis-(4-piperidinopiperidino)dicyanoquinodimethane (4-PPDQ)[**2**]. Compounds **1** and **2** showed very striking and impetuous results. Both compounds exhibited helical supramolecular assemblies, high fluorescence in their solid state and as well large stokes shift of about ~95 nm. Quantum yield of solids was 14 times elevated than their solutions. Scanning electron microscope images revealed microstructures of dendrites, spheres and ring like morphologies.

1. Introduction

Molecules and materials possessing fluorescent nature are of great interest in a wide variety of applications. They serve as potential candidates for developing display devices and some of them are choices for sensor applications. Organic dyes and pigments are important for paints, inks, LCD and OLED's etc. Molecular recognition events which trigger fluorescence response are effectively exploited in chemical and biological applications. Molecules with efficient fluorescence include, aromatic hydrocarbons and their derivatives, azines, azomethines, several six and five membered heterocyclic derivatives, carbonyl compounds and metal complexes with a wide range of organic ligands [1,2]. Organic liquids, polymers, sol–gel systems and variety of nano materials also display strong fluorescence [1,3–5]. The gel networks consisting of molecules with π-electrons are known to exhibit enhanced fluorescence through gelation process [6,7]. Several molecular crystals [8–11] over the past decades have been developed for optical and non-linear optical applications. Molecular materials possessing strong fluorescence are also being developed for their luminescent applications [1,12]. Inquisition in the field of medicine and biology make use of fluorescent materials. Dansyl chloride, fluorescein and rhodamine derivatives were used as antibody tracers [1,13]. Fluorescein and its derivatives [14,15] are most widely used as diagnostic tools as they can be injected into the body and their luminescence demonstrates patency of blood vessels, blood supply to various parts of grafted skin, the boundaries of affected area etc. Photodynamic therapy [16] used for the treatment of cancer is also concerned with design of molecules which can potentially bind with DNA and cleave the duplex under visible and illumination light.

Self-assembly plays a vital role in the design of functional molecular materials [17–20]. Molecular adducts are well known potential candidates usually formed by self-assembly process [21–24]. Fascinated by the helical super structures present in the biological systems with their unique functions, helical supramolecular assemblies were designed with the help of various type of interactions like weak interactions, π–π, Van der Waals and hydrogen bonding. Self-assembled helical fibers and aggregation enhanced fluorescence was observed in triphenylbenzene discotic derivatives in their gel phase [25]. Hydrogen and ionic bonded helical columns was observed in a solid state fluorescent host system [26] prepared by combining two molecules. Thus the self-assembled supramolecules reported were either salts or co-crystals

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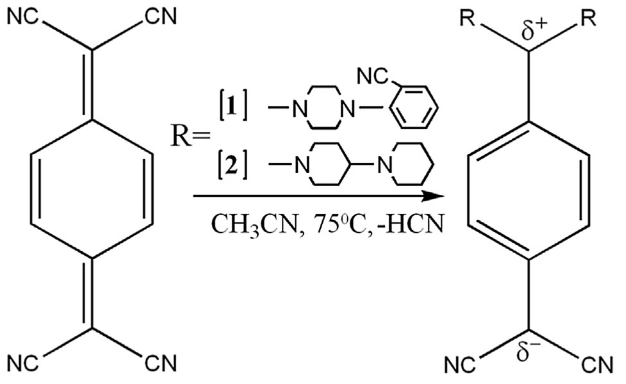

Scheme 1. 1,2-CPP and 4-PP bis-substituted tetracyanoquinodimethanes.

or of those that were mostly obtained from gels. Some of them showed enhanced fluorescence through aggregation. Its noteworthy, that single molecules in bis-substituted tetracyanoquinodimethanes possessing supramolecular helical self-assemblies with large stokes shift have not been reported so far. The heterocyclic building blocks, piperidines [27,28] and piperazines [29,30] are found in biologically active compounds across a number of various therapeutic areas. The piperidine ring can be recognized in more than half of the alkaloids that are known till today, and also in several natural or synthetic compounds. These are the moieties in cancer treatment drugs [27–30]. The crystal structure of an anticancer prodrug having piperidinopiperidine moiety had a major role in enzyme inhibition which indicate the binding affinity with active sites of proteins [31,32].

Molecules with delocalized π-electron systems, donor–acceptor structures possess very interesting optical characteristics. Tetracyanoquinodimethane (TCNQ), a strong π-electron acceptor is of immense interest in molecular electronics [33,34]. A class of bis-substituted zwitterionic TCNQ molecules called as diaminodicyanoquinodimethanes (DADQ's) have been synthesized with their interest in non-linear optical properties [35–39] and some of them showed dramatic enhancement of light emission in the solid state [40] when compared to the solution state, where the remote functionalities played the key role of molecular organization. Design of molecules and their supramolecular structures with shape and interactions is always challenging as it leads to the ease in flexibility and fabrication of the desired molecular materials for their applications as dyes and pigments. Crystal structures and morphologies of several dyes and pigments are not studied in detail.

There is a continuous interest in the design of optical molecular materials. We have studied the impact of 1,2-CPP and 4-PP through substitution on TCNQ. This resulted in two distinct compounds 1,2-CPPDQ [**1**] and 4-PPDQ [**2**], exhibiting *unique features such as* supramolecular helical self-assemblies, large stokes shift, solution and solid state enhanced fluorescence and *certain interesting morphologies* when compared to some of the earlier known bis-substituted TCNQ's that were especially focussed on non-linear optical properties. The above mentioned results reveal their probable application as unique fluorescent organic dyes as well as pigments due to their enhanced fluorescence in solutions and solids, possessing π–π interactions. Molecular dipole alignment in their crystal structures also gives insight into their applicability in the field of non-linear optical molecular materials.

2. Materials and methods

2.1. Synthesis of 1 and 2

Compounds **1** and **2** were synthesized according to the procedure reported [41,42] with minor modifications (Scheme 1). 0.08–0.1 g (4.8–5.7 mmol) of substituted amine (1,2-CPP and 4-PP) was added to a warm solution of 0.05–0.06 g (2.4–2.8 mmol) of TCNQ in 15 mL of acetonitrile, (CAUTION: HCN is liberated) the solution turned dark green immediately and changed to yellow (Scheme 1) subsequently yellow crystalline products **1** and **2** formed in about 45 min. The reaction mixture was stirred for 45 min more at 75 °C to ensure the completion of reactions. Microcrystalline precipitate obtained was recrystallized in acetonitrile. Crystals of **1** were obtained through evaporation from the solvent mixture of

Table 1
Crystallographic information and structure refinement for **1** and **2**.

Empirical formula	$C_{32}H_{28}N_8$	$C_{32}H_{50}N_6O_2$
Formula weight	524.62	550.78
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic
Space group	C 1 2/c 1	Pbcn
Unit cell dimensions	$a = 26.186(4)$ Å, $\alpha = 90°$ $b = 12.1362(9)$ Å, $\beta = 107.702(16)°$ $c = 27.886(4)$ Å, $\gamma = 90°$	$a = 22.6303(16)$ Å, $\alpha = 90°$ $b = 12.0419(10)$ Å, $\beta = 90°$ $c = 11.1878(7)$ Å, $\gamma = 90°$
Volume	8442.5(18) Å^3	3048.8(4) Å^3
Z	12	4
Density (calculated)	1.238 Mg/m^3	1.200 Mg/m^3
Absorption coefficient	0.077 mm^{-1}	0.076 mm^{-1}
F(000)	3312	1200
Crystal size	0.38 × 0.28 × 0.18 mm^3	0.38 × 0.32 × 0.18 mm^3
Theta range for data collection	2.76–23.25°	3.07–25.00°
Index ranges	$-29 \leq h \leq 19$, $-13 \leq k \leq 9$, $-24 \leq l \leq 30$	$-26 \leq h \leq 26$, $-10 \leq k \leq 14$, $-13 \leq l \leq 8$
Reflections collected	13517	7533
Independent reflections	6056 R(int) = 0.1140	2695 R(int) = 0.0557
Completeness to theta = 23.25° (1) and 25.00°(2)	99.8%	99.9%
Data/restraints/parameters	6056/0/544	2695/0/186
Goodness-of-fit on F2	0.858	1.052
Final R indices $I > 2$sigma(I)	$R1 = 0.0670$, w$R2 = 0.0814$	$R1 = 0.0662$, w$R2 = 0.1501$
R indices (all data)	$R1 = 0.2125$, w$R2 = 0.1263$	$R1 = 0.1198$, w$R2 = 0.1801$
Extinction coefficient	0.00022(2)	0.0031(8)
Largest diff. peak and hole	0.182 and −0.184 e Å^{-3}	0.185 and −0.256 e Å^{-3}