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Note

Anion controlled structural variation of silver(I) coordination polymers with a new donor–π–acceptor ligand

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ABSTRACT

A new ligand with D–π–A symmetry has been synthesized in high yield by Knoevenagel condensation of 4-(dimethylamino)benzaldehyde with malononitrile. The ligand forms coordination polymers with Ag(I) salts at room temperature where the ultimate structure is dependent upon the counter anion. With $AgNO_3$, a 2D tubular structure is formed where the nitrate anions bridge two Ag(I) centers. When $AgBF_4$ is used, a 1D grid structure results but with AgOTf, a 1D zigzag structure is formed. Thus, anions control the structure of the coordination polymers formed. Each coordination polymer affords high TPA activity that can be correlated with the structure of the polymer.

1. Introduction

The design and synthesis of coordination polymers have received enormous attention in recent years due to their potential applications [1] in diverse areas. Formation of these structures depend on several factors: (i) stereoelectronic molecular information encoded in the ligand(s), (ii) reading-out this information by metal ions with preferences for coordination numbers as well as stereochemistry, and (iii) the conditions used for the synthesis. The counter anions can also control the ultimate structure [2] of the coordination polymer. Efforts have been directed towards the synthesis of coordination polymers exhibiting large second order bulk optical nonlinearity [3]. However, polymers that exhibit large third order optical nonlinearity are still very rare. Recent studies show that metal clusters and polymers in DMF/DMSO solution exhibit third-order NLO responses by measuring the effective third-order NLO absorption coefficient (α_2) and refractive index (η_2) with nanosecond laser pulses [4]. Third order optical nonlinearity can be evaluated in terms of two photon absorption (TPA) cross-section (σ_2) [5]. Molecules having extended π-conjugation with symmetrical charge transfer and increased dimensionality (1D to 3D) are expected [6] to have significant TPA cross-section. Herein, we report a ligand with donor–π–acceptor structural motif that itself shows a low σ_2 value but on making coordination polymers with Ag-salts exhibit significantly large σ_2 values measured by femtosecond open-aperture Z-scan technique at 880 nm. We show that the counter anion controls the ultimate polymeric structure thereby varying the possible charge transfer symmetry as well as dimensionality and associated σ_2 value. Materials exhibiting large two-photon absorption cross-section are important for their potential use in several areas of bio-photonics and materials science [7].

2. Experimental

2.1. Materials

Reagent grade 4-(dimethylamino)benzaldehyde, malononitrile, piperidine and the silver salts were from Aldrich while the solvents were from SD Fine Chemicals, India. All solvents were purified prior to use while the rest of the chemicals were used as received.

2.2. Physical measurements

Spectroscopic data were collected as follows: IR (KBr disk, 400–4000 cm^{-1}) Perkin–Elmer Model 1320. Microanalyses for the compounds were obtained from the Central Drug Research Institute, Lucknow, India. ESI-MS data were acquired on a MICROMASS QUATTRO Quadruple Mass Spectrometer. ^1H NMR spectra recorded on a JEOL JNM-LA400 FT (400 MHz) instrument in $CDCl_3$ with Me_4Si as internal standard. Melting points were recorded with an electrical melting point apparatus by PERFIT, India and are uncorrected.

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2.3. Synthesis

2.3.1. Ligand **L**

The ligand **L** is synthesized in ~90% yield as a yellow solid by Knoevenagel condensation of 4-(dimethylamino)benzaldehyde with malononitrile in dry ethanol. To a solution containing 0.15 g (1 mmol) of 4-(dimethylamino)benzaldehyde and 0.1 g (1.5 mmol) of malononitrile in 10 ml dry ethanol, two drops of piperidine are added. After 30 min of stirring at room temperature, a deep yellow solid formed that is collected by filtration, washed with ethanol and finally dried under vacuum. Yield 92%. M.pt. 150 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ (ppm) 3.12 (s, 6H), 6.68 (d, 2H), 7.44 (s, 1H), 7.79 (d, 2H). ESI-mass *m/z* (%): 196 (80). *Anal.* Calc. for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.30. Found: C, 73.12; H, 5.73; N, 21.41%.

2.3.2. Synthesis of $\{Ag(L)NO_3\}_n$

A solution of $AgNO_3$ (0.17 g; 1 mmol) in ethanol (5 ml) is added slowly and carefully on the top of the layer of a solution of **L** (0.2 g; 1 mmol) in dichloromethane (10 ml) in a crystallization tube. Single crystals in the form of red blocks are obtained after standing for 2 days at room temperature. Yield 52%. *Anal.* Calc. for $C_{12}H_{11}N_4O_3Ag$: C, 39.26; H, 3.02; N, 15.26. Found: C, 39.34; H, 3.16; N, 15.38%.

2.3.3. Synthesis of $\{Ag(L)_2BF_4\}_n$

This complex is synthesized following the above procedure replacing $AgNO_3$ by $AgBF_4$. Yellow rectangular single crystals are isolated after standing for a week at room temperature. Yield 43%. *Anal.* Calc. for $C_{24}H_{22}BF_4N_6Ag$: C, 48.93; H, 3.76; N, 14.26. Found: C, 48.99; H, 3.87; N, 14.35%.

2.3.4. Synthesis of $\{Ag(L)CF_3SO_3\}_n$

A solution of CF_3SO_3Ag (0.26 g; 1 mmol) in benzene (10 ml) is added slowly and carefully on the top of a 10 ml dichloromethane solution of **L** (0.2 g; 1 mmol) in a crystallization tube. After standing at room temperature for 7 days, orange rectangular crystals of the title compound can be isolated in 47% yield. *Anal.* Calc. for $C_{13}H_{11}N_3O_3SF_3Ag$: C, 34.38; H, 2.44; N, 9.26. Found: C, 34.35; H, 2.55; N, 9.32%.

2.3.5. X-ray structural studies

Single crystal X-ray data on **1**–**3** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and the structures were solved and refined as described earlier [8]. The crystal and refinement data are collected in Table 1 while selective bond distances and angles are given in Table 2. Several non-bonding interactions are shown in Table 3.

Table 1
Crystallographic data and details of the refinement procedure for **1**–**3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{12}H_{11}AgN_4O_3$	$C_{24}H_{22}AgBF_4N_6$	$C_{13}H_{11}AgF_3N_3O_3S$
Formula weight	367.12	589.16	454.18
Radiation, wavelength (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/n$
a (Å)	8.831(5)	19.772(5)	6.745(5)
b (Å)	7.911(5)	8.047(5)	14.702(5)
c (Å)	19.094(5)	15.202(5)	16.022(5)
β (°)	97.70	99.22(5)	101.68(5)
V (Å^{-3})	1321.9(1)	2387.5(2)	1555.9(1)
Z	4	4	4
D_{calc} (g cm^{-3})	1.845	1.450	1.939
Size (mm^3)	0.18 × 0.16 × 0.14	0.15 × 0.13 × 0.11	0.17 × 0.15 × 0.13
T (K)	100(2)	100(2)	100(2)
μ (mm^{-1})	1.537	0.888	1.481
Reflections measured	3243	2939	3844
Reflections used [$I \geqslant 2\sigma(I)$]	2934	2316	3304
Parameters	185	169	221
Goodness-of-fit (GOF) on F^2	1.019	1.307	1.030
Final *R* indices [$I \geqslant 2\sigma(I)$]	R_1 = 0.0308, wR_2 = 0.0723	R_1 = 0.0812, wR_2 = 0.1827	R_1 = 0.0322, wR_2 = 0.0756
R indices (all data)	R_1 = 0.0351, wR_2 = 0.0741	R_1 = 0.1051, wR_2 = 0.2307	R_1 = 0.0402, wR_2 = 0.0786
Maximum/minimum residual (e Å^{-3})	1.172/−0.492	1.439/−1.812	0.818/−0.371
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2

Table 2
Selected bond distances (Å) and bond angles (°) for **1**–**3**.

1					
Ag1···N2	2.373(2)	Ag1···Ag1	7.024(3)	O2···Ag1···O3	50.78(3)
Ag1···N3	2.289(2)	N2···Ag1···O2	94.72(5)	O2···Ag1···O1	94.83(9)
Ag1···O1	2.500(2)	N2···Ag1···O1	75.17(7)	O1···Ag1···O3	128.20(7)
Ag1···O2	2.607(2)	N3···Ag1···O1	120.19(9)	N2···Ag1···N3	94.97(8)
Ag1···O3	2.444(2)	N3···Ag1···O3	100.75(8)		
2					
Ag1···N1	2.139(5)	Ag1···Ag1	8.047(3)	N1···Ag1···N2′	79.95(5)
Ag1···N2	2.833(2)	N1···Ag1···N2	100.05(5)		
3					
Ag1···N1	2.196(2)	N1···Ag1···N3	138.95(8)	N3···Ag1···O3	113.45(7)
Ag1···N3	2.169(2)	N1···Ag1···O3	97.63(7)		
Ag1···O3	2.3791(19)				

Table 3
6 Geometrical parameters for various noncovalent interactions found in **2** and **3**.

Interaction		D^a (Å)	d^b (Å)	θ^c (°)
2				
C(Ar)–H···F	F2···H3	3.385(3)	2.461(4)	172.41(2)
C(sp^2)–H···F	F3···H9	3.089(3)	2.315(4)	131.58(5)
C(sp^3)–H···F	F3···H15A	3.385(5)	2.470(3)	159.30(4)
	F2···H1A	3.748(5)	2.883(2)	150.36(7)
	F2···H1C	3.387(4)	2.816(3)	118.98(4)
Ag···C(arene)	Ag1···C3	3.249(5)		
	Ag1···C4	3.055(4)		
3				
C(Ar)–H···O	O2···H3	3.486(5)	2.696(3)	143.39(2)
	O2···H5	3.460(7)	2.535(4)	173.16(3)
C(sp^2)–H···O	O1···H9	3.282(2)	2.616(2)	130.48(5)
C(sp^3)–H···O	O1···H8A	3.332(6)	2.415(3)	159.78(4)
C(sp^2)–H···F	F2···H9	3.412(3)	2.621(3)	145.44(3)
C(sp^3)–H···F	F3···H7C	3.468(7)	2.570(4)	155.74(2)
Ag···C(arene)	Ag1···C2	2.746(5)		
	Ag1···C2	2.871(6)		

[a] *D* is the distance between C and the acceptor (C, O or F atom).
[b] *d* is the distance between H and the acceptor (C, O or F atom).
[c] θ is the angle at H in C–H···X (X = C, O or F atom).

2.3.6. TPA cross-section measurements

The TPA cross-section (σ_2) values are measured by using a standard open aperture z-scan technique [9] for 1 cm long quartz sample cells. We have used 150 fs pulses at 880 nm with 76 MHz repetition rate from mode-locked tunable Coherent Mira titanium: sapphire laser (Model 900) which is pumped by Coherent Verdi frequency doubled Nd: vanadate laser. The experimental procedure followed as described earlier [10]. All of the compounds were measured at 5×10^{-4} M solution in DMF solvent. The solvent itself does not show any TPA activity under experimental conditions. The open-aperture traces for the polymers are given as Supporting information. We have taken Rhodamine 6G for which the σ_2 value is known in the literature [11] as the reference for calibrating our measurement technique. The low solubility of the complexes in THF and their insolubility in low boiling organic solvents do not allow for making thin films of the polymers for solid-state TPA measurements.

3. Results and discussion

All the coordination polymers possess high stability towards light and air. They are moderately soluble in DMF, DMSO and slightly soluble in THF.

Single crystal X-ray diffraction studies reveal that structure of **1** consists of planar dimeric [Ag_2L_2] units where each metal is coordinated to two CN groups from two ligands and three O atoms from two NO_3^- ions in a distorted square-pyramidal geometry. The dimeric units are repeated via bridging nitrates forming a 2D network (Fig. 1). The *N*,*N*′-dimethylbenzene moieties align perpendicularly on both side of the crystallographic *bc* plane at an approximate distance of 7.911 Å from each other signifying absence of any significant interactions. All Ag–N bond distances found in **1** are within the normal range observed in other –CN donor ligands complexed with Ag(I) [12]. The two Ag–$O_{nitrate}$ bond lengths (2.607 and 2.501 Å) are slightly longer than those observed in other nitrate bridged Ag(I) complexes [13]. The Ag···Ag separation in the dimeric unit is 7.024 Å.

Due to non-coordinating nature of BF_4^- counter anion, each Ag(I) ion in **2** is tetra-coordinated in a square planar geometry with coordination from four CN groups belonging to four different ligands propagating the polymeric chain along the crystallographic *b* axis. While viewing down the crystallographic *a* axis, it looks like a grid structure (Fig. 2).

The BF_4^- anions occupy the space between two 1D polymeric chains joining them via C(sp^3)–H···F and C(sp^2)–H···F hydrogen bonding interactions (Table 3) to form a 2D hydrogen bonded network structure. Each 2D network is packed on top of another via Ag–C(arene) interactions (3.055, 3.249 Å) and C(sp^2)–H···F hydrogen bonding interactions (Table 3). The Ag–C interactions are considerably greater than the limits (2.47–2.76 Å) commonly observed in Ag(I)–aromatic complexes [14].

In **3**, each Ag(I) ion is tri-coordinated with ligation from two CN donors belonging to two different ligands and one O atom of the $CF_3SO_3^-$ counter anion. The two CN groups of each ligand bind two metal ions thereby propagating the 1D coordination polymeric chain along the crystallographic *c* axis in a zigzag fashion (Fig. 3). The *N*,*N*′-dimethylbenzene moieties are oriented perpendicular to this chain on either side of the polymeric chain in an alternate fashion. These 1D chains are arranged parallel to one another with considerable Ag–C(arene) and C–H···F interactions (Table 3). There are also considerable interlayer C–H···O interactions involving O atom of $CF_3SO_3^-$ anion and the ligand. The Ag–C contacts (2.746, 2.871 Å) are slightly greater than the limits (2.47–2.76 Å) commonly observed in Ag(I)–aromatic complexes. Thus, the benzene ring in **3** coordinates to the Ag(I) ion with an η^2 bonding mode, which is normally observed in arene–metal complexes [14].

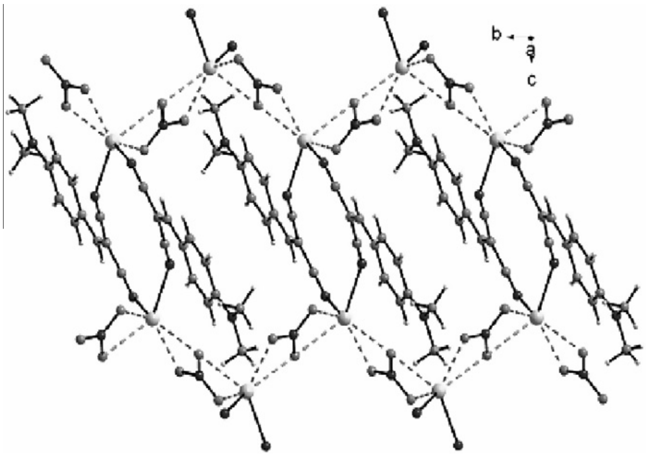


Fig. 1. A perspective view of the 2D network in **1**.

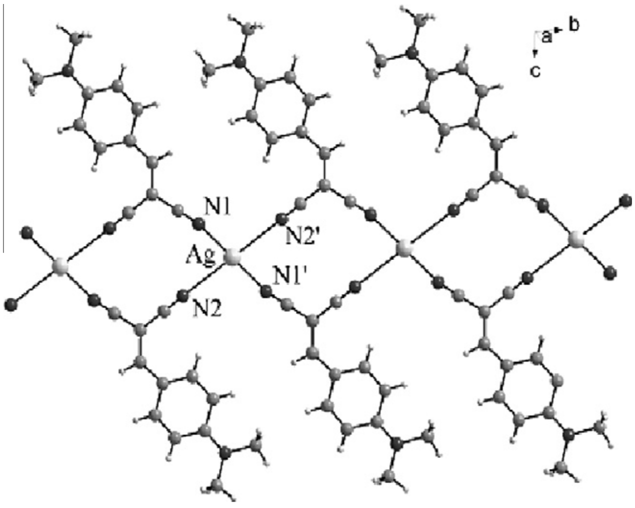


Fig. 2. A perspective view of the grid structure in **2**.

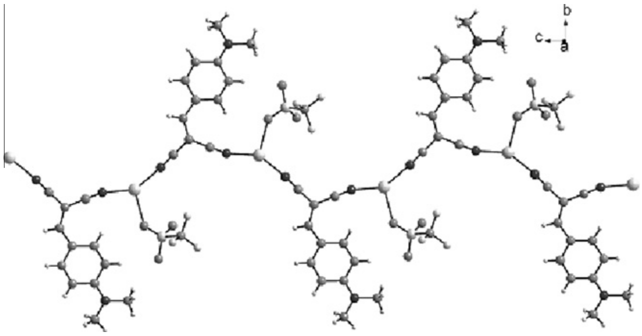
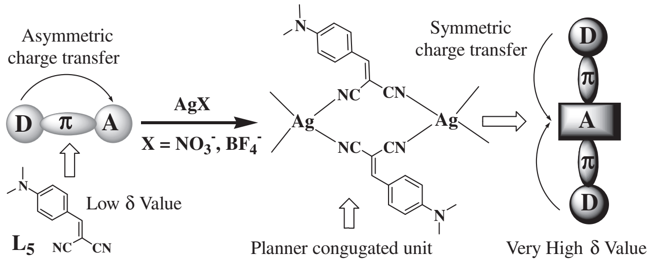


Fig. 3. A perspective view of the zigzag structure of **3**.



Scheme 1. Schematic representation of Ag(I) coordination polymer based on D–π–A NLO-phore for enhanced TPA activity.

The ligand **L** exhibits a broad and intense intra-ligand charge transfer (ILCT) band at λ_{max} = 435. This band is red-shifted with increased ε value upon complexation with Ag(I)–ion depending on the polymeric structure. The nonlinear optical measurements are performed in DMF solution in the near-infrared region since it is clear from the UV–Vis spectra that the ligand (**L**), solvent and all the coordination polymers (**1**–**3**) are transparent in this region. The free ligand **L** exhibits σ_2 value of 200 GM at 880 nm while **1**–**3** show much higher TPA activity at the same wavelength with the magnitude of σ_2 value depending on the structure of the coordination polymer. The σ_2 value for **2** and **3** are found to be 1150 and 1040 GM, respectively, while **1** shows $\sigma_2 = 1800$ GM. The increased dimensionality in **1** could be possibly the factor responsible for higher TPA cross-section [6a]. The σ_2 value of **2** is larger than that of **3** which can be attributed to the formation of more symmetric D–π–A–π–D unit (Scheme 1) in the former.

In conclusion, we have synthesized various Ag(I) coordination polymers based on D–π–A NLO-phore for enhanced two-photon absorption cross-section values. The TPA efficiency depends upon the structure of the polymeric architecture which is controlled by the counter anion of the Ag(I) salt. Further studies are in progress on other systems in our laboratory.

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Appendix A. Supplementary material

CCDC 617604, 617605 and 617606 contain the supplementary crystallographic data for **1**–**3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.03.003.

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