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Structural, spectral, electrochemistry, thermal properties and theoretical studies on 4-[N, N-di(4-tolyl)amino] benzaldehyde -2-chloro benzoylhydrazone



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HIGHLIGHTS

- 4-[N, N-di(4-tolyl)amino] benzaldehyde-2-chloro benzoylhydrazone were synthesized and characterized.
- The photophysical, thermostability properties of the titled compound were found to be distinctively modified by benzoylhydrazone structure.
- DFT calculations and experimental results were coincided on structure, energy gap and electrochemistry.
- The hydrogen bonding interactions within sheets and π - π interactions 3D network confirmed the title compound can be used as amorphous material in nonpolar solvents.

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ABSTRACT

The title compound 4-[N, N-di(4-tolyl)amino] benzaldehyde-2-chloro benzoylhydrazone (C₂₈H₂₄ClN₃O, M_r = 453.96) was synthesized by the reaction of 4-[N, N-di(4-tolyl)amino] benzaldehyde with 2-chlorobenzohydrazide, and its structure was characterized by IR, ¹H NMR, ¹³H NMR, high-resolution mass spectrometry and single-crystal X-ray diffraction. The crystal belongs to Monoclinic, space group P2(1)/n with a = 12.626(3), b = 12.609(3), c = 15.837(3)Å, $\beta = 90.00(3)^\circ$, Z = 5, V = 2512.5(9)Å³, $M_r = 453.95$, Dc = 1.280 g/cm³, $\mu = 0.183$ mm⁻¹, F(000) = 1024, R = 0.0432 and wR = 0.1087. X-ray analysis revealed that one of the benzene ring and acylhydrazone were essentially planar, the 2-chloro benzene ring and amide were non-planar, the torsion angles C(1)–C(6)–C(7)–O(1) and C(5)–C(6)–C(7)–O(1) are 61.4(5)° and -114.4(4)°. The thermal stability studies indicate that the title compound is stable up to 341.1 °C. The spectral, electrochemistry properties and theoretical studies show that the title compound is a good candidate for the charge-transporting materials.

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Introduction

In the process of the large-scale manufacturing of the opto devices, amorphous molecular materials used as hole-transport materials must be capable of forming uniform amorphous thin films by either vacuum deposition or spin coating from solution. Triphenylamine-based hydrazones used as organic hole-transport materials have been widely studied [1–6]. Up to now, the efforts have been laid on developing solution processable organic small molecules, for that they offer the advantages of simple

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preparation/purification procedures, lower cost and the high reproducibility in the performance of the device. The recent extensive studies have revealed that small triphenylamine-based molecules can also form stable amorphous glasses above room temperature if their molecular structures are properly designed [7–9]. The following strategies have been adopted for this purpose [1]: (1) Molecules should possess nonplanar molecular structures; (2) The incorporation of bulky and heavy substituents leads to enhanced stability of the resulting amorphous glasses; (3) The introduction of structurally rigid moieties can increase the thermal stability. In our concept, we designed the triphenylamine-based hydrazones which the enlarged system of conjugated π -electrons of the target molecular would reinforce the inclination of the molecules to form glasses and would allow enhanced charge-carrier mobilities. On the other hand, the presence of hydrazide and cholro

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Scheme 1. Synthesis route of the compound III.



Fig. 1. Molecular structure of the compound III.

Table 1

Selected optimized and experimental geometries parameters of the title compound in ground state.

Bond lengths (Å)	Exp./cal.	Bond lengths (Å)	Exp./cal.	Bond lengths (Å)	Exp./cal.
Cl(1)C(1) O(1)C(7) N(1)C(7) N(1)N(2) N(1)H(1) N(2)C(8) N(3)C(12) N(3)C(12) N(3)C(15)	$\begin{array}{c} 1.737(3)/1.772\\ 1.228(4)/1.220\\ 1.354(4)/1.377\\ 1.393(3)/1.361\\ 0.901(10)/1.017\\ 1.289(4)/1.287\\ 1.406(4)/1.411\\ 1.425(4)/1.425\\ 1.439(4)/1.425 \end{array}$	C(1)-C(2) C(1)-C(6) C(2)-C(3) C(2)-H(2) C(6)-C(7) C(8)-C(9) C(8)-H(8) C(9)-C(10) C(10)-C(11)	1.391(5)/1.396 1.392(5)/1.404 1.372(5)/1.392 0.9500/1.085 1.510(5)/1.516 1.448(4)/1.458 0.9500/1.100 1.405(4)/1.404 1.376(4)/1.389	$\begin{array}{c} C(10)-H(10)\\ C(11)-C(12)\\ C(15)-C(16)\\ C(16)-C(17)\\ C(16)-H(16)\\ C(17)-C(18)\\ C(17)-C(18)\\ C(18)-C(21)\\ C(21)-H(21A) \end{array}$	0.9500/1.088 1.404(4)/1.406 1.387(5)/1.403 1.387(5)/1.392 0.9500/1.086 1.391(5)/1.401 1.507(5)/1.511 0.9800/1.095
Angle (°)	Exp./cal.	Angle (°)	Exp./cal.	Angle (°)	Exp./cal.
$\begin{array}{c} C(7)-N(1)-N(2)\\ C(7)-N(1)-H(1)\\ N(2)-N(1)-H(1)\\ C(8)-N(2)-N(1)\\ C(12)-N(3)-C(22) \end{array}$	119.5(3)/119.2 122(2)/120.0 118(2)/119.2 113.9(3)/116.6 123.2(3)/120.4	$\begin{array}{c} C(12)-N(3)-C(15)\\ C(22)-N(3)-C(15)\\ C(2)-C(1)-Cl(1)\\ C(6)-C(5)-H(5)\\ C(1)-C(6)-C(7) \end{array}$	118.2(3)/120.5 116.9(2)/119.1 118.7(3)/115.9 119.7/117.0 122.7(3)/128.8	O(1)C(7)N(1) O(1)C(7)C(6) N(2)C(8)C(9) N(2)C(8)H(8)	125.5(3)/123.4 121.6(3)/120.5 121.7(3)/122.1 119.2/121.3
Torsion angle (Å)	Exp./cal.	Torsion angle (Å)	Exp./cal.	Torsion angle (Å)	Exp./cal.
$\begin{array}{c} C(7)-N(1)-N(2)-C(8)\\ Cl(1)-C(1)-C(6)-C(7)\\ N(2)-N(1)-C(7)-O(1)\\ N(2)-N(1)-C(7)-C(6)\\ C(1)-C(6)-C(7)-O(1) \end{array}$	177.9(3)/179.6 7.1(4)/8.9 2.9(5)/3.9 -172.6(3)/-179.6 61.4(5)/31.0	$\begin{array}{c} N(1)-N(2)-C(8)-C(9)\\ N(2)-C(8)-C(9)-C(10)\\ C(8)-C(9)-C(10)-C(11)\\ C(22)-N(3)-C(12)-C(13)\\ C(15)-N(3)-C(12)-C(13) \end{array}$	-178.8(3)/-179.9 -14.6(5)/-0.41 177.9(3)/179.6 16.5(5)/34.0 -147.9(3)/-145.1	$\begin{array}{c} C(12)-N(3)-C(15)-C(20)\\ C(22)-N(3)-C(15)-C(20)\\ C(12)-N(3)-C(15)-C(16)\\ C(22)-N(3)-C(15)-C(16)\\ C(5)-C(6)-C(7)-O(1) \end{array}$	-130.3(3)/-135.7 64.3(4)/65.1 51.3(4)/45.6 -114.1(3)/-115.2 -114.4(4)/-116.7

Exp./cal. = experimental/calculated.

Table 2

UV-visible, fluorescence, electrochemical, thermogravimetric analysis measurements for compounds I-III and the corresponding HOMO and LUMO energies and HOMO-LUMO gaps (E_{e}).

Compound	Ι	П	III
$\lambda_{abs} (nm)^{a}$	302	360	375
$\epsilon (10^4 \mathrm{M}^{-1} \mathrm{cm}^{-1})^{\mathrm{b}}$	4.53	2.86	3.40
$\lambda_{em} (nm)^{c}$	k	547	499
Δ (nm) ^d	1	58	73
$\lambda_{onset} (nm)^{e}$	336	683	595
E_{g} (eV, opt) ^f	3.69	1.82	2.08
E _{ox} ⁱ (V, CV) ^g	0.79	1.03	1.00
Е_{номо} (eV, CV) ^h	-5.53	-5.77	-5.74
E_{LUMO} (eV, CV) ^h	-1.84	-3.95	-3.66
Е_{НОМО} (eV, DFT) ⁱ	-5.62	-5.81	-5.86
Е_{LUMO} (eV, DFT) ⁱ	-1.42	-3.56	-3.47
E_{g} (eV, DFT)) ⁱ	4.20	2.25	2.39
T_{d} (°C) ^j	234.1	273.9	341.1

^a Absorption maximum in CH₂Cl₂ solution.

^b The molar extinction coefficient at λ_{max} in CH₂Cl₂ solution.

^c Emission maximum in CH₂Cl₂ solution.

^d The red-shift compared with I.

^e The bond edges in the UV-visible absorption spectra of the sample.

^f Obtained from UV-visible spectra: $E_{g} = 1240/\lambda_{onset}$.

^g Obtained from the cyclic voltammograms (in CH₂Cl₂ (10^{-3} M), using n-Bu₄-NClO₄ as support electrolyte (10^{-1} M), scan rate: 50 mV s⁻¹ versus SCE).

^h Determined from the onset of the oxidation peak: $E_{HOMO} = -E_{ox}e - 4.74e$; $E_{IIIMO} = E_{HOMO} + E_{\pi} [21,22].$

ⁱ Calculated by the **DFT** calculations at B3LYP/6-31(d) level.

^j Decomposition temperature.

k Undetected.

¹ Undetermined.



Fig. 2. The hydrogen-bonded monolayer network of the compound III.

groups should make it to be nonplanar molecular structures. Furthermore, it is very important to understand the electrochemical properties of the triphenylamine-based model molecules, which will help us to design suitable monomer and permit tuning of the redox potentials of the molecular. In this paper, a new compound containing triphenylamine and benzoic hydrazide substituted by chloro units has been synthesized (Scheme 1), its structure was analyzed by X-ray diffraction and its photophysical, electrochemistry, thermal properties were also evaluated.

Experiments

The melting point was determined on an X-6 binocular microscope apparatus and the thermometer was uncorrected. Infra-red spectra were obtained on a Bio-rad Fts3000 spectrometer in the



Fig. 3. Hydrogen bonding interactions within sheets and π - π interactions 3D network of the compound III.



Fig. 4. UV-visible absorption spectra and fluorescence spectra of III.

4000–400 cm⁻¹ range as KBr disks. ¹H and ¹³C NMR were measured on a Bruker AC-P500 Instrument (400 MHz) with CDCl₃ as the solvent and TMS as the internal standard. High-resolution mass spectrometry (HRMS) data were recorded on VG ZAB-HS mass spectrometer. The single-crystal structure was determined on a Bruker SMART 1000 CCD diffractometer. Thermogravimetric analysis (TGA) was performed on TA Q500 in a nitrogen atmosphere at a heating rate of 5 °C/min. UV-visible absorption spectra were recorded on a Perkin Lambda25 spectrophotometer. Cyclic voltammetry (CV) was done on a CHI 7600 electrochemical work-station with Pt plate, Pt wire, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively.

All reagents, unless otherwise specified, were obtained from FengChuan Chemical Co. and used as received.

Synthesis of 4-[N, N-di(4-tolyl)amino] benzaldehyde-2-chloro benzoylhydrazone (III)

Intermediate 4-[N, N-di(4-tolyl)amino] benzaldehyde I was synthesized from N, N-di(4-tolyl) aniline according to the reference [10]. 2-chlorobenzohydrazide II was synthesized according to the literature [11] (ESI-MS(m/z, $[M+H]^+) = 171.2$). The title compound 4-[N, N-di(4-tolyl)amino] benzaldehyde-2-chloro benzoylhydrazone III was obtained as the following description. 4-[N, N-di(4-tolyl)amino] benzaldehyde I (0.57 g, 1.9 mmol) was dissolved in 8 mL ethanol at room temperature. Then

2-chlorobenzohydrazide II (0.21 g, 1.9 mmol) and acetic acid (20 µL) was added. The reaction mixture was completed by stirring for 24 h at room temperature (indicated by TLC). The product was precipitated out of the solution. The solid was collected, washed with methanol and dried to obtain the title compound **III** as a yellow solid in 36% yield (the yield was not optimized). Melting point 111.8–112.5 °C; IR(KBr, cm⁻¹): 3441, 3186, 3026, 2920, 1657, 1598, 1558, 1505, 1290, 816. ¹H NMR (CDCl₃, 400 MHz, ppm): 8.09 (s, 1H, -N=CH-), 7.72 (t, 1H), 7.56 (d, 1H, J = 8.8 Hz), 7.44–7.27 (m, 3H), 7.22 (d, 1H, J = 8.8 Hz), 7.10–7.00 (m, 6H), 6.96–6.93 (m, 3H), 6.85 (d, 2H, J = 8.8 Hz), 2.31 (s, 6H, $-CH_3$); ¹³C NMR (CDCl₃, 100 MHz, ppm): 150.6, 144.9, 144.4, 133.8, 133.6, 131.7, 130.1, 130.0, 129.0, 128.6, 128.2, 127.2, 126.4, 125.6, 125.4, 20.9, 20.8; HR-ESI-MS (m/z, [M+H]⁺) calcd. for C₂₈H₂₅ON₃Cl⁺ 454.1681, found 454.1682.

Crystal data and structure determination

The colorless crystal of the title compound with dimensions of $0.20 \text{ mm} \times 0.18 \text{ mm} \times 0.12 \text{ mm}$ was selected for X-ray diffraction analysis. The data were collected by a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromatic Mo K α radiation (λ = 0.71073 Å) using a φ - ω scan mode at 113(2) K. In the range of $2.06 \le \theta \le 25.02^\circ$, a total of 20,599 reflections were collected with 4447 unique ones (Rint = 0.0378), of which 3800 were observed with $I > 2\sigma(I)$ and used in the succeeding refinements. Intensity data were corrected for Lp factors and empirical absorption. The structure was solved by direct methods and expanded by difference Fourier techniques with SHELXS-97 program [12]. All the non-hydrogen atoms were located with successive difference Fourier syntheses. The structure was refined by full-matrix least-squares techniques on F^2 using anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms bonded to C atoms were located geometrically and treated using a riding model, with C–H = 0.95-1.00 A and $U_{iso}(H) = 1.2$ or 1.5 $U_{eq}(C)$. The final refinement gave R = 0.0432, wR = 0.1087, $w = 1/[s^2(Fo^2) + (0.0677P)^2 + 0.3002P]$ where $P = (Fo^2 + 2F_c^2)/3)$, S = 1.080, $(\Delta \rho)$ max = 0.374, $(\Delta \rho)$ min = -0.475 e/A⁻³.

Results and discussion

Structure description of the compounds

The ¹H NMR, ¹³C NMR, IR and HR MS analysis for the molecular **III** are in good agreement with the title compound. In order to unambiguously confirm the structure of the product, the single



Fig. 5. The optimized geometries of the III calculated with DFT on the B3LYP/6-31G(d) level.



Fig. 6. Multiple cyclic voltammograms scans of I(A), II(B), III(C) (cycle 1st to 10th).

crystal of **III** was analyzed by X-ray diffraction apparatus. The molecular structure is shown in Fig. 1. The selected bond lengths and bond angles are listed in Tables 1 and 2.

The geometry of the N(3) atom is a distorted tetrahedral configuration with the C(12)—N(3)—C(22), C(12)—N(3)—C(15) and C(22) -N(3)—C(15) angles of 123.2(13)°, 118.23(13)° and 116.79(12)°. The configuration of π cross section (—C==N) is basically a plane

with the N(1)–N(2)–C(8)–C(9) torsion angle of $-178.8(3)^{\circ}$. The torsion angles of N(2)–N(1)–C(7)–O(1), N(2)–N(1)–C(7)–C(6) and O(1)-C(7)-C(6)-C(1) is $3.1(3)^{\circ}$, $-173.54(14)^{\circ}$, $60.9(2)^{\circ}$, respectively, which suggests that the nitrogen atom N(1) is not placed at the same plane with the phenyl ring substituted by chlorine atom and the plane of hydrazone structure. The dihedral angle between the -C=N moiety and the plane of carbonyl group (O(1)-C(7)-N(1)) is 125.23(15)°. The torsion angles of C(5)-C(6)-C(7)-O(1) is $-115.08(19)^\circ$, so the carbonyl group is not placed at the same plane with the phenyl ring substituted by chlorine atom. No direct π - π interactions are observed among all moieties in the unit cell. Therefore, the cross-link part of target compound is non-planar. It can be seen from Table 2 that all the bond lengths of C--C are located between the normal C=double bond (1.34 Å) and C–C single bond (1.54 Å), which show that III has a highly delocalized π -electron system in the molecule. N(1)–C(7) (1.3470(2) Å) and N(2)–N(1) (1.3883(18) Å) bonds are slightly shorter than the typical C–C bond (1.54 Å) [13] and C–N bond (1.47 Å) [14], the typical N–N bond (1.44 Å) and N=N bond (1.24 Å) [15], respectively, suggesting the N–C and N–N bonds have partial double bond character.

The packing of **III** in methanol is shown in Figs. 2 and 3. The interaction between the methanol molecule and **III** is reinforced by the formation of the hydrogen bond N(1)—H···O(2) and O(2)—H···O(1). The titled molecules form strong hydrogen bond interactions with the methanol molecules forming infinite 1D chains. These chains are inter-linked via N—H···O and O—H···O interactions involving carbonyl groups/amide groups to form 2D independent sheets cross-linked via one methanol molecule (Fig. 2). In Fig. 3, there are some intermolecular weak π – π interactions between the two **III** species, with the separation between the two benzene planes titled as C9—C10—C11—C12—C13—C14 being 3.7790 Å (center to center), 3.4571 Å (center to plane), respectively. The π -interactions are hence crucial for the crystal packing stabilization. These weak interactions are largely responsible for the thermodynamic stability of the crystal system.

Photophysical properties of III

The UV-visible absorption spectra and fluorescence spectra of compound I–III (4×10^{-5} M in CH₂Cl₂) are shown in Fig. 4. Broad absorption bands covering the wavelength range from 250 to 450 nm can be observed for all compounds, the λ_{max} exhibits red-shifted by roughly 73 nm when going from I to III. This trend is in agreement with the trend previously reported in the case of homologous series of conjugated triphenylamine-core hydrazones [16]. This red-shift can be related to the geometrical changes that occur in the longest conjugated chain length composed by the planarization of C(8)–C(9)–N(1)–N(2)–C(7)–O(1) when comparing the geometries to the structure of I which, consequently, improves the π -conjugation and decreases the **HOMO-LUMO** gaps. Compound III has two absorption peaks (λ_{max}) at 296 and 375 nm which can be assigned to the π - π^* absorption of the molecule [17–19], which is similar to that of **II**. Also, the molar extinction coefficients in dilute CH2Cl2 solution was calculated as $3.40\times 10^4 M^{-1}\ cm^{-1}\ (\lambda_{max}$ = 375 nm) for III. The optical band gaps (E_g) are calculated as 2.08 eV for III. The fluorescence spectra of the title compound shows a emission peak wavelength at 499 nm excited by 380 nm. The maximum emission bonds of I-III in fluorescence spectra exhibit the trend of II > III (compound I was not excited by 380 nm), and III show a stronger intensity when the length of the conjugated system is increased, exhibiting emission maxima ranging from 547 nm for II to 499 nm for III. The molecule **III** exhibits a broad absorption range and a relatively low band gap, which would be in favor of light-harvesting when used as the active-layer material in optical devices.



Fig. 7. HOMO and LUMO pictograms for compounds I-III (A); comparison of the electrochemical and theoretical (B3LYP/6-31G(d) level) HOMO and LUMO energies of compounds I-III(B).

Electronic structure and electrochemical properties

To gain insight into the geometrical properties and scrutinize the charge transfer on excitation, the ground-state geometries of the III had been optimized in the gas phase by DFT with the Gaussian03 package, using the hybrid B3LYP functional and the standard 6-31G(d) basis set before the beginning of experimental synthesis of III (Fig. 5). The optimized parameters (bond lengths, bond angles and dihedral angles) of the title compound were listed in Table 1. A global comparison was performed by superimposing the molecular skeletons obtained from X-ray diffraction and the theoretical calculations. Compared with the experimental data for the title compound, it is well known that DFT optimized bond lengths, bond angles and dihedral angles show the strongest correlation with the experimental values (Table 1). Although the largest difference between experimental and calculated torsion angle is about $61.4(5)^{\circ}/31.0^{\circ}$ for C(1)-C(6)-C(7)-O(1), $-14.6(5)^{\circ}/-0.41^{\circ}$ for N(2)-C(8)-C(9)-C(10), the same trend was coincided between the real structure and DFT optimized structure. According to those results, the optimized geometry is obtained for molecule **III** coincides with the crystalline structure of **III**.



Fig. 8. TGA of the compound III.

Due to the energy levels in the organic semiconductors are of great importance, density functional theory (DFT, B3LYP/6-31(d) level) methods and cyclic voltammetry was performed to investigate the electrochemical properties and HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels of compounds I-III. The HOMO energy levels with respect to the vacuum level correspond to the oxidation potential (E_{ox}). Based on the optimized geometry at the B3LYP/ 6-31G(d) level, we have designed, synthesized, investigated and calculated triphenylamine-based organic charge transferring materials. The experimental data and calculation of the E_{HOMO} , E_{LUMO} and E_{g} were shown schematically in Figs. 6 and 7 and Table 2. Our calculations of I-III reveal the HOMO electron density mainly localized on the TPA core and the LUMO electron density mainly localized on the conjugated moiety to the TPA core in II and III. Compared with that of I, adding -C=O- and -C=N conjugated structure to the TPA core in II/III makes the HOMO(LUMO) energies increase (decrease) resulting in decreasing HOMO-LUMO $gaps(E_g: I > III > II)$. In spite of the differences between the theoretical and electrochemical values, the same trends are obtained from the B3LYP calculations and the electrochemistry measurements. The differences between the theoretical and electrochemical values maybe cause by a well-known consequence of performing calculations that lack medium-related factors [20]. The multiple cyclic voltammograms are shown in Fig. 6. The oxidation potential and current retain their shapes (I, III) under multiple continuous potential scans, while the oxidation current envelope of II grows with successive potential scans. The III exhibited one quasi-reversible reduction peaks characteristic for triphenylamines. It is obvious that III shows a good electrochemical stability to be similar to those of I, II, and the lowest HOMO value (-5.74 eV) being close to that (5.30 eV) of the NPD materials [19] currently used in charge-transporting layer. In spite of this, the smaller energy gap of III show the titled compound to be a good candidate for charge-transporting materials.

Theamal properties of III

The thermal properties of the **III** was tested by the **TGA** analysis (Fig. 8). The samples were heated from 25 to 800 °C in a nitrogen flow with a heating rate of 10 °C min⁻¹. Fig. 8 shows that the maximum weight loss located at 341.1 °C indicating that **III** has a good thermal stability. Compared with that of **I** and **II** (T_d : 234.1 °C for **I**,

273.9 °C for II), the TGA results of III show that the model compound has enough resistance against thermal decomposition, which is due to the presence of the acylhydrazone structure in the compound III.

Conclusions

A novel compound 4-[N. N-di(4-tolvl)amino] benzaldehvde-2chloro benzovlhvdrazone was synthesized and characterized by IR. HRMS. ¹H NMR and ¹³C NMR. The single crystal was cultivated and analyzed by single-crystal X-ray diffraction. In the crystal structure, the chloro substituted benzoylhydrazone moiety leads to the non-planar structure formation and modified the photophysical, and thermal properties of the titled compound. The thermal and electrochemistry stability of the title compound has been studied, and the most weight was lost when the temperature is at 341.1 °C. The titled compound as charge-transfer materials and ligand precursors for the generation of new metal complexes would extend these materials promising for optical devices. The packing structure of III in methanol show that the compound III used as amorphous material should avoid to be dissolved in alcohol or polar solvents. As it was already mentioned in the comparison between the experimental and theoretical study, the DFT calculations was used to assist designing some triphenylaminebased derivatives was in progress.

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