The hydroxylic position mediated the luminescent properties based on 4amino-4H-1,2,4-triazole: syntheses, crystal structures and Hirshfeld analyses

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## Graphical abstract



### The hydroxylic position mediated the luminescent properties based on

### 4-amino-4H-1,2,4-triazole: syntheses, crystal structures and Hirshfeld analyses

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### Abstract

of compounds based 4-amino-4*H*-1,2,4-triazole namely, Α set on group, x,x'-(4-amino-4H-1,2,4-triazole-3,5-diyl) diphenol [x=2 (1), x=3 (2), x=4 (3)], were obtained through reacting a set of cyano-phenol and hydrazine under the solvothermal conditions, respectively. The title compounds 1-3 have been characterized by IR, element analysis (EA), single crystal X-ray diffraction, and powder X-ray diffraction (PXRD). A lot of hydrogen bonds (C/N/O-H···O/N) and C-H··· $\pi$  can be clearly observed in these compounds. It surprisedly occurs the presence of *trans*- and *cis*-conformation for compounds **3**. The increasing order of the dihedral angles between the phenyl and triazole-yl rings is 1 < 2 < 3. The solid-state luminescent spectra of 1-3 show that the emission maxima are observed at 461, 414 and 402 nm, respectively, which shows the declining order of 1>2>3. The luminescent maximal peaks decrease with the diminution of hydroxylic steric effects.

The Hirshfeld surface analyses reveal that the contribution order of the  $O \cdots H/H \cdots O$  contacts in compounds 1-3 is listed: 1<2<3, which is in a good agreement with that of the dihedral angles, and an inverse proportional to the fluorescent maxima of compounds 1-3.

**Keywords**: 4-Amino-4*H*-1,2,4-triazole; Crystal structures; Supramolecular interactions; Hirshfeld surface analysis; Dihedral angles

### 1. Introduction

The triazole-based derivatives are one of the most significant N-heterocyclic compounds and have extensively applied in the fields of materials and medicine [1-15] [16-19] [20-21], which can be assigned to their strong coordination abilities and important biologically activities. Among these triazole-containing compounds, the derivatives based on amino-1,2,4-triazole nuclei show interesting properties such as optics, gas absorption and magnetism [22-27]. Recently, the composite consisting of nickel flakes on 4-amino-4H-1,2,4-triazole/graphene has been designed for sustainable hydrogen evolution in acid and alkaline media [28]. 3,5-Diaryl-4-amino-1,2,4-triazole derivatives have been used as effective corrosion inhibitors for steel in acid solution [29]. Nickel clusters with amino-1,2,4-triazole scaffold have been proved to have good catalysis for ethene [30]. Additionally, 4-amino-1,2,4-triazole have been proved to play pivotal roles in anti-cancer cells and various types of anti-disease in the human body [31]. However, it still remains unexplored for the luminescent moieties materials with 4-amino-1,2,4-triazole though derivatives containing some amino-1,2,4-triazole have been synthesized [32-33]. Very importantly, it is urgent to design and investigate the derivatives based on 4-amino-1,2,4-triazole skeleton with the controllable photoluminescent behaviours through the position of substituted functional groups.

Based on these elegant works mentioned above, in this contribution, we would like to report a set of 4-amino-1,2,4-triazole functional groups, namely, x,x'-(4-amino-4H-1,2,4-triazole-3,5-diyl) diphenol [x=2 (1), x=3 (2) and x=4 (3)], were obtained through reacting a set of cyano-phenol and hydrazine under the solvothermal conditions, respectively. The single crystal structures of 1-3 have been discussed, their photoluminescent properties and thermal behaviors were investigated in details. As we expected, the hydroxylic position can obviously control the luminescent properties of these amino-triazole derivatives, which can be further confirmed by the Hirshfeld surface analyses. To our best knowledge, there is not the record of the tunable luminescent behaviors of compounds containing amino-4H-1,2,4-triazole through the position of the substituted functional groups.

### 2. Experimental

### 2.1 Materials and measurements

The reagents and solvents employed were used as received without further purification. Elemental analyses were performed on an Elementar vario EL III microanalyser. The FT-IR spectra were recorded from KBr pellets in the range 400-4000 cm<sup>-1</sup> on a Bruker spectrometer. The absorption spectra were recorded with an absorption spectrophotometer model TU-1900/1901. Thermogravimetric analysis (TGA) data were collected with a TA SDT Q600 analyzer in N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup> in the range of 20-600 °C. The solid–state fluorescence spectra were recorded on a HITACHI–4500 spectrometer at room temperature.

### 2.1. The synthesis of compound 1.

To a mixture solution of ethylene glycol (10 mL) and 85% hydrazine hydrate (3.8 mL, 60 mmoL), 2-hydroxybenzonitrile (1.180 g, 10 mmoL) were heated at 130 °C for 3 days in a 15 ml Teflon-lined vessel container. Then an ice water (30 ml) was added to the cooled reaction mixture.

The production was filtered and dried. The sample (0.134 g, 0.5 mmol) was dissolved in methanol (5 ml). The solution was stood for one week. Brown block crystals suitable for X-ray diffraction were collected by vacuum filtration. Yield: 0.100 g, 75%. M.p. 258-260 °C. Elemental analysis calcd (%) for  $C_{14}H_{12}N_4O_2$  (268.28): C, 62.68; H, 4.51; N, 20.88; Found: C, 62.53; H, 4.52; N, 20.79. IR (KBr, cm<sup>-1</sup>): 3333(s), 3287(w), 3224(w), 3076(w), 2914(w), 2677(w), 2554(w), 1962(w), 1933(w), 1634(s), 1608(s), 1525(w), 1483(s), 1457(m), 1422(w), 1381(s), 1292(m), 1278(w), 1268(w), 1249(s), 1227(m), 1171(w), 1162(w), 1153(w), 1134(w), 1109(w), 1095(w), 1008(m), 971(w), 950(w), 948(w), 829(w), 754(vs), 702(m), 692(m), 650(w), 607(m), 559(w), 533(w), 490(w), 471(w), 458(m), 430(vw).

### 2.2. The synthesis of **2**.

The synthesis procedure of compound **2** was similar to that of compound **1** when the 3-hydroxybenzonitrile took place of 2-hydroxybenzonitrile. The orange block crystals were collected. Yield: 0.221 g, 70%. M.p. 289-291°C. Elemental analysis calcd (%) for  $C_{31}H_{36}N_8O_7$  (632.68): C, 58.85; H, 5.74; N, 17.71; Found: C, 58.71; H, 5.73; N, 17.74. IR (KBr, cm<sup>-1</sup>): 3354(w), 3327(w), 3189(w), 1589(s), 1528(m), 1487(m), 1458(s), 1435(w), 1333(w), 1313(m), 1286(m), 1241(w), 1223(w), 1203(w), 1146(w),1170(w), 1158(w),1137(w), 1090(w), 1075(w), 1037(w), 995(s), 978(w), 944(s), 888(s), 788(s), 724(s), 690(s), 633(w), 538(w), 472(w), 447(w), 412(w).

### 2.3. The synthesis of compound 3

The synthesis procedure of compound **3** was similar to that of compound **1** when the 4-hydroxybenzonitrile took place of 2-hydroxybenzonitrile. The colorless needle crystals were collected. Yield: 0.107 g, 80%. M.p. 298-300 °C. Elemental analysis calcd (%) for  $C_{14}H_{12}N_4O_2$  (268.28): C, 62.68; H, 4.51; N, 20.88; Found: C, 62.79; H, 4.50; N, 20.82. IR (KBr, cm<sup>-1</sup>): 3476(b),

3416(s), 3223(m), 2809(w), 2678(w), 2509(w), 2362(w), 1915(w), 1772(w), 1613(s), 1481(s), 1363(m), 1236(s), 1173(s), 1108(m), 979(m), 902(m), 842(s), 744(m), 671(w), 598(m), 534(s), 453(w).

### 2.4. Single-crystal structure determination

Single-crystal structures of compounds 1-3 were measured by a Bruker Smart CCD equipped with graphite-monochromator Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The lattice parameters were obtained by a least-squares refinement of the diffraction data. All the measured independent reflections were used in the structural analysis, and semi-empirical absorption corrections were applied using the SADBASE program [34]. The program SAINT was used for integration of the diffraction profiles [35]. The structure was solved by direct methods using the SHELXS and OLEX2 program of the SHELXTL package and refined with SHELXL [36-38]. All non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for all the non-hydrogen atoms based on  $F^2$ . The hydrogen atoms were placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. Special computations for the crystal structure discussions were carried out with PLATON for Windows. A summary of the crystallographic data and structure refinements are listed in Table 1. Selected bond lengths and bond angles are summarized in Table 2. Corresponding hydrogen bond and packing interactions data for compounds 1-3 are listed in Tables 3 and 4, respectively. Other parameters of compounds 1-3 are presented in Table 5.

### 2.5. Hirshfeld surface analyses

The Hirshfeld surface were calculated by the program of CrystalExploer [39-40]. The

contribution of the bond contacts was listed in Table 6.

### 3. Results and discussion

### 3.1. Description of the crystal structures

### 3.1.1. Structure of 2,2'-(4-amino-4H-1,2,4-triazole-3,5-diyl)diphenol (1).

Single X-ray crystallographic analysis results reveal that compound **1** belongs to the  $P2_12_12_1$  space group with the orthorhombic crystal system. In the unsymmetric unit, there is only one 2,2'-(4-amino-4*H*-1,2,4-triazole-3,5-diyl) diphenol (**2OH**) molecule (Fig. 1a). The bond lengths and the bond angles containing the amino-triazole group is analogous to those observed in other triazole-based moieties. The dihedral angle between the phenyl rings and the triazole one can be found to be  $13.0(1)^{\circ}$  and  $50.2(1)^{\circ}$ , where the former is significantly smaller than the latter. The observed results can be assigned to the presence of intramolecular hydrogen bonds. The present value is obviously lower/higher than those in the literature.

The supramolecular structures mainly rely on intermolecular hydrogen bonds and the C-H $\cdot\pi$  packing interactions. As shown in Fig. 1, the responding interactions are described as the following: (a) The O-H $\cdot$ N (O1–H1 $\cdot\cdot\cdot$ N1<sup>*a*</sup>, 2.703(2) Å, <sup>*a*</sup>-x,1/2+y,-1/2-z) intermolecular hydrogen interconnects occur between the oxygen atoms from the hydroxylic groups and the triazole-yl nitrogen atoms. (b) There exist the weak C4–H4 $\cdot\cdot\cdot$ Cg1<sup>*b*</sup> (3.563(2) Å, <sup>*b*</sup>-x,-1/2+y,-1/2-z) packing interactions, where the Cg1 represents the center of the triazole-yl ring. The adjacent **2OH** molecules alternatively arrange into a supramolecular one-dimensional (1D) chain along the crystallographic *b* axis through the O1–H1 $\cdot\cdot\cdot$ N1<sup>*a*</sup> intermolecular hydrogen bonds and the C4–H4 $\cdot\cdot$ Cg1<sup>*b*</sup> packing interactions (Fig. 1b). (c) The C3–H3 $\cdot\cdot$ Cg3<sup>*a*</sup> (3.374(2) Å, <sup>*a*</sup>1/2+x,-3/2-y,-z; Cg3=C9–C10–C11–C12–C13–C14) and the C12–H12 $\cdot\cdot\cdot$ Cg2<sup>*c*</sup> (3.480(2) Å, <sup>*c*</sup>-1/2-x,-1-y,1/2+z; Cg2=C1–C2–C3–C4–C5–C6) can be discovered, which

connects the adjacent 1-D chains. As a result, a two-dimensional (2-D) supramolecular layer is built along the crystallographic *bc* plane (Fig. 1c). (d) The N–H··O (N4–H4A····O2<sup>*b*</sup>, 3.135(2) Å, <sup>*b*</sup>1+x,y,z) intermolecular hydrogen bonds derive from the amino-nitrogen atoms and the another hydroxylic oxygen atoms. Based on the hydrogen bonds, the adjacent 2D sheets can extend into a three-dimensional (3-D) supramolecular architecture along the crystallographic *a* direction (Fig. 1d). Notably, there does not exist the stacking interactions among the aromatic rings, where the shortest distance can be observed to be 4.1313(12) Å.

### 3.1.2Structure description of 3,3'-(4-amino-4H-1,2,4-triazole-3,5-diyl)diphenol (2)

When 3-hydroxy-benzonitril replaced 2-hydroxy-benzonitril, compound 2 cam be generated under the similar reaction conditions. Single X-ray crystallographic analysis reveals that compound 1 crystallizes in the orthorhombic crystal system with the  $P2_12_12_1$  space group. The unsymmetric unit contains two 3,3'-(4-amino-4*H*-1,2,4-triazole-3,5-diyl)diphenol (**3OH**) molecules and three methanol molecules (Fig. 2a and Table 1). Notably, it happens two different isomers for **3OH** molecules. One is *trans*-isomer; another is *cis*-isomer. In *trans*-**3OH** structure, the dihedral angles with 28.5(1)° and 36.5(1)° can be found between the triazole ring and phenyl groups. In *cis*-**3OH** structure, there exist the dihedral angles with 28.4(1)° and 36.7(1)° among the aromatic rings, which are comparable to those found in the *trans*-**3OH**. The observed values are larger than that  $(13.0(1)^\circ)$ found in **2OH** structure and are smaller than that  $(50.2(1)^\circ)$  observed in **2OH** molecule. The bond lengths and the bond angles around the triazole-core is normal, which are similar to those observed in other triazole-based compounds.

Generally, it often happens the hydrogen bonds and the packing interactions in the supramolecular structures. In compound **2**, there exist many kinds of hydrogen bonds as the following: (a) The

O-H…N (O2-H…N1<sup>a</sup> 2.763(3) Å, <sup>a</sup>1/2+x,3/2-y,1-z; O3-H3…N6<sup>b</sup> 2.662(3) Å, <sup>b</sup>-1/2+x,1/2-y,1-z) intermolecular hydrogen bonds can be found. The former originates from the oxygen atoms and the nitrogen atoms of the triazole-yl group in the trans-3OH molecules; while the latter does from the oxygen atoms and the nitrogen atoms of in the *cis*-**3OH** molecules. (b) The N-H…N (N4-He…N2<sup>a</sup> 3.380(3) Å, <sup>a</sup>1/2+x,3/2-y,1-z) intermolecular hydrogen interactions derive from the triazole-yl and amino nitrogen atoms in trans-30H molecules. (c) The C-H…N (C20-H20…N5<sup>b</sup> 3.432(4) Å,  $^{b}$ -1/2+x,1/2-y,1-z) intermolecular hydrogen bonds occur between the phenyl carbon atoms and the triazole-yl nitrogen atoms of *cis*-**3OH** molecules. The C4-Hl···N4 and C20-H20···N8 (3.015(5) and 3.096(5) Å, respectively) intramolecular hydrogen interactions become from the phenyl carbon atoms and the amino-nitrogen atoms in *trans*-**30H** molecules. (d) The C-H···O (C18-H18···O1<sup>d</sup>) 3.273(4) Å,  $^{d}1+x,y,z$  intermolecular hydrogen connections produce between the phenyl carbon atoms of cis-3OH skeleton and the oxygen atoms of trans-3OH molecules. The C30-Hs $\cdots$ O2<sup>e</sup> 3.392(5) Å,  $e^{1/2-x,1-y,1/2+z}$  intermolecular hydrogen bonds stem from the carbon atoms of the guest methanol and the oxygen atoms of the cis-3OH molecules. (e) The O-H…O (O1-Ha…O5 2.658(4) Å, O6-Hb...O3 2.733(3) Å, O4-H4...O7 2.640(4) Å) hydrogen bonds originate from the oxygen atoms of the **3OH** hosts and the methanol molecules. The O-H···O (O5-Hc···O6<sup>b</sup> 2.789(3) Å, <sup>b</sup>-1/2+x,1/2-y,1-z; O7-Hd···O6<sup>c</sup> 2.798(3) Å, <sup>c</sup>1/2-x,1-y,-1/2+z) intermolecular interactions emerge from the oxygen atoms of different methanol molecules. (f) The N4-Hf...O4 hydrogen bonds with the distance of 3.042(4) Å can be found, which happen between the amino-nitrogen atom from the cis-3OH and the hydroxylic oxygen atoms from the trans-3OH moieties. Apart from hydrogen bonds mentioned above, the packing interactions also made a significant contribution in crystal structure. The packing interactions can be observed in structure 2: (i) it occurs the  $\pi^{-}\pi$  packing

interactions such as Cg1····Cg6<sup>*d*</sup> (<sup>*d*</sup>-1/2+x,3/2-y,1-z), Cg2····Cg4<sup>*b*</sup> (<sup>*b*</sup>-1/2+x,1/2-y,1-z), Cg4····Cg2<sup>*e*</sup> (<sup>*e*</sup>1/2+x,1/2-y,1-z) as well as Cg6····Cg1<sup>*a*</sup> (<sup>*a*</sup>1/2+x,3/2-y,1-z), where the bond distances are 3.506(2), 3.594(2), 3.594(2) and 3.506(2) Å, respectively. The Cg1, Cg2, Cg4 and Cg6 indicate the centers of the triazole-yl and phenyl rings, respectively. (ii) The C-H··*π* interactions occur too, for examples, C31-Ho··Cg5<sup>*c*</sup> (<sup>*c*</sup>1/2-x,1-y,-1/2+z) and C29-Hw··Cg2<sup>*f*</sup> (<sup>*f*</sup>-x,-1/2+y,3/2-z) with the distance of 3.739(4) and 3.355(4) Å, respectively.

It is obvious that it happens the  $\pi \cdot \pi$  and C-H $\cdot \pi$  packing interactions (Cg1 $\cdots$ Cg6<sup>d</sup>, Cg2 $\cdots$ Cg4<sup>b</sup>, C31-Ho $\cdots$ Cg5<sup>c</sup> and C29-Hw $\cdots$ Cg2<sup>f</sup>) accompanying with hydrogen interactions (intramolecular C4-HI $\cdots$ N4, intermolecular O5-Hc $\cdots$ O6<sup>b</sup> and C20-H20 $\cdots$ N8 hydrogen interactions), which connects **3OH** molecules and the guest methanol molecules. As a result, a supramolecular1-D chain is built along the crystallographic *b* axis (Fig. 2b), where the guest methanol molecules decorate the supramolecular chain. Further, the O1-Ha $\cdots$ O5, O6-Hb $\cdots$ O3, O4-H4 $\cdots$ O7 and C30-Hs $\cdots$ O2<sup>e</sup> intermolecular hydrogen bonds make every two neighboring supramolecular 1-D chains expand into a supramolecular 2-D waveform layer along the crystallographic *bc* plane (Fig. 2c). The host **3OH** molecules align in the formation of herringbone. Finally, the supramolecular 2-D sheets extend into a supramolecular 3-D framework along the crystallographic *a* direction through the O2-H $\cdots$ N1<sup>a</sup>, O3-H3 $\cdots$ N6<sup>b</sup>, O7-Hd $\cdots$ O6<sup>c</sup>, N4-He $\cdots$ N2<sup>a</sup>, N4-Hf $\cdots$ O4, C18-H18 $\cdots$ O1<sup>d</sup> and C20-H20 $\cdots$ N5<sup>b</sup> intermolecular hydrogen interconnections (Fig. 2d).

To further investigate the interactions between the host and the guest, the related figures can be drawn. As shown in Figs. 2b-2d, there exist the strong hydrogen bonds (O1-Ha···O5 and O4-H4···O7) between the methanol molecules and the host skeleton, where two methanol molecules act as the acceptor of hydrogen bonds and **3OH** molecules do as the donor of the hydrogen bonds.

Another methanol molecule plays a role in the donor of the hydrogen bonds (O6-Hb···O3), where the acceptor of the hydrogen bonds is one *trans*-**3OH** molecule. Meanwhile, this methanol molecue (O6) acts as the acceptor of the hydrogen bonds (O7-Hd···O6<sup>c</sup> and O5-Hc···O6<sup>b</sup>), where other two methanol molecules (O5 and O7) serve as the donors of the hydrogen bonds. In order to consolidate the interactions between the host and the guest, we can find that the weak hydrogen bonds of C30-Hs···O2<sup>e</sup> and the packing interactions of C31-Ho··Cg5<sup>c</sup> and C29-Hw···Cg2<sup>f</sup> can be observed.

3.1.3 Structure description of 4,4'-(4-amino-4H-1,2,4-triazole-3,5-diyl)diphenol) (3)

When 4-hydroxy-benzonitril took place of 2-hydroxy-benzonitril, compound **3** can be generated under the similar reaction conditions. The single X-ray crystallographic diffraction results indicate that the compound **3** crystallizes in the orthorhombic  $P2_1/n$  group. The asymmetric unit consists of one 4,4'-(4-amino-4*H*-1,2,4-triazole-3,5-diyl)diphenol molecule (**4OH**) (Fig. 3a and Table 1). Noteworthy, the dihedral angle between the triazole-yl and the phenyl rings can be observed to be  $38.3(1)^{\circ}$  and  $41.3(1)^{\circ}$ , which are higher than those found in compound **2**.

Generally, there exist the supramolecular interactions (hydrogen bonds,  $\pi \cdot \pi$  and C-H  $\cdot \pi$  packing) in the supramolecular architectures. In compound **3**, two kinds of interactions can be observed to be intermolecular hydrogen bonds and C-H  $\cdot \pi$  packing interactions (Fig. 3, Tables 3-4). As shown in Fig. 3, it occurs the O-H  $\cdot \cdot \cdot N$  (O1-H1 $\cdot \cdot \cdot N2^a$  ( $^a$ -1+x,y,z), O2-H2 $\cdot \cdot \cdot N1^b$  ( $^b$ 1/2+x,3/2-y,1/2+z) and O2-H2 $\cdot \cdot \cdot N2^b$ ) intermolecular hydrogen contacts, which become from the hydroxylic oxygen atoms and the triazole-yl nitrogen atoms from the **4OH** molecules. The bond distances are 2.794(3), 2.833(3) and 3.302(3) Å, respectively. The hydrogen bonds of N4-H4A $\cdot \cdot O2^c$  ( $^c$ 2-x,1-y,1-z) and N4-H4B $\cdot \cdot O1^d$  ( $^d$ 1/2-x,1/2+y,1/2-z) can also be found, which happen between the amino N atoms and the hydroxylic O atoms from the **4OH** skeleton. The bond lengths are 3.267(3) and 3.245(3) Å,

respectively. Obviously, each **4OH** molecule makes use of the hydrogen bonds of O2-H2···N1<sup>*b*</sup> and O2-H2···N2<sup>*b*</sup> hydrogen bonds to form the head-hail mode, which results into building a 1-D supramolecular chain (Fig. 3b). Then, through these hydrogen bonds the neighboring supramolecular 1-D chains can extend into a supramolecular 2-D laminated structure along the crystallographic *ac* plane (Fig. 3c). Except from the intermolecular hydrogen bonds, the C-H··π packing interactions also play a key role in strengthening the stabilities of the supramolecular structures. The C-H··π packing interactions are summarized as the following: C3-H3··Cg2<sup>*a*</sup> (<sup>*a*</sup>1/2-x,1/2+y,1/2-z) and C5-H5··Cg3<sup>*b*</sup> (<sup>*b*</sup>3/2-x,-1/2+y,1/2-z), where the bond separation is 3.573(3) and 3.302(3) Å, respectively. Both the Cg2 and Cg3 rings represent the centers of the phenyl rings. Based on the intermolecular hydrogen interactions of N4-H4A···O2<sup>*c*</sup> and N4-H4B···O1<sup>*d*</sup> and C-H··π packing interactions of C3-H3···Cg2<sup>*a*</sup> directions of C3-H3···Cg2<sup>*a*</sup> and C5-H5···Cg3<sup>*b*</sup>, a 3-D supramolecular framework can be generated along the crystallographic *a* direction (Fig. 3d). Interestingly, the smallest stacking distance with the distance of 3.8222(18) Å can be found between two phenyl rings (Table 5).

### 3.3. IR spectra

The IR spectra of compounds 1-3 containing amino-triazole moiety are shown in Fig. 4. As shown in Fig. 4, the characteristic bands of the amino/hydroxylic groups are observed at 3333, 3413 and 3416 cm<sup>-1</sup> for compounds 1-3, respectively. It happens the bands located at 1608 and 1483 cm<sup>-1</sup>, 1589 and 1487 cm<sup>-1</sup>, 1613 and 1481 cm<sup>-1</sup> for 1-3, respectively, which indicates the stretching vibration of aromatic C=C and C=N. There exist the peaks observed at range of 971-754, 978-724, and 979-744 cm<sup>-1</sup> for compound 1-3, respectively, suggesting the existence of the in-plane and out-plane bending vibration of  $\gamma_{(CH)}$  and  $\delta_{(CH)}$  modes of phenyl rings.

### 3.4. Thermogravimetric analysis

To study the thermal stabilities of the title compounds, thermogravimetric analyses (TGA) were carried out [41]. The experiments were performed on samples containing numerous single crystals under a  $N_2$  atmosphere with a heating rate of 10 °C min<sup>-1</sup> (Fig. 5). The TGA curves of compounds **1** and **3** reveal that it happens a platform found at about 290 °C, showing that there exists high thermal stability for compounds **1** and **3**. The present results indicate that there exist strong hydrogen bonds among compounds **1** and **3**. Then, it occurs to start the weight loss up to 295 and 320 °C for compounds **1** and **3**, respectively, which can be assigned to the decomposition of the organics. For compound **2**, the TGA curve shows that it happens a weight loss at range of 75-150 °C, suggesting the departure of the crystallized methanol molecules (cald. 15.1%, obsd. 9.0%). The observed results reveal that it occurs the strong hydrogen bonds between the host and the guest molecules. Then, a plateau can be found at the range of 150-325 °C. After that, the weight loss can be observed, indicating the decomposition of organic skeleton.

In order to investigate the relationship between the thermal stabilities and the molecular structures, we carefully check the supramolecular interactions of these compounds. In compounds **1** and **3**, the whole molecule shows the *trans*-isomer and *cis*-isomer features, respectively, which leads to the low decomposition temperature (295 and 320  $^{\circ}$ C, respectively). However, in compound **2**, we can observe the existence of *cis*-isomer and *trans*-**3OH** structures, which accounts for the high thermal stabilities (decomposition temperature of 325  $^{\circ}$ C).

### 3.5. Luminescent properties

To investigate the luminescent properties of the title compounds, the solid-state photoluminescent spectra of **1-3** were performed at room temperature [42-43]. As shown in Fig. 6, the emission peaks can be found at 461, 414 and 402 nm for compounds **1-3**, respectively, when the

excitation wavelengths are 350, 320 and 300 nm for compounds 1-3, respectively. The observed results may be attentively ascribed to the  $\pi^* \rightarrow \pi$  or  $\pi^* \rightarrow n$  transitions [44-50]. Notably, there exist an order of the maximal peaks for these compounds: 1>2>3. Interestingly, we can find that compounds 1-3 have different position for the -OH group connected to the phenyl rings, and their position changes from *orth-*, *meta-* to *para-*location. It happens an order of the steric effects for the hydroxylic groups: 1>2>3. As discussed above, we can find that in compound 1, there exists the big conjugation system originated from the phenyl and triazole-yl rings with the dihedral angle of 63.3° (Table 5). In compounds 2 and 3, the dihedral angles are 65.0° and 79.6°, respectively, suggesting the conjugation degree decreases, which results into a blue phenomenon. Obviously, the order of the dihedral angles is listed: 1<2<3, which is an inverse-proportional to that of the maximal peaks. Thus, we can conclude that the luminescent maximal bands decline down the steric effects for the hydroxylic groups. Thus, the photoluminescent behaviors can be controlled by the hydroxylic position.

### 3.6. Hirshfeld surface analysis

To further quantitatively evaluate the relationship between the intermolecular interactions and the properties for these compounds, the Hirshfeld surface analyses were performed [51-53]. The Hirshfeld surface and the corresponding finger print plots were used to visualize the intermolecular interactions of the compounds **1-3**. The Hirshfeld surface mapped over the  $d_{norm}$  (normalized connect distance, which equal to the Van der Walls radii),  $d_i$  (the distance from the distance from the nucleus to the nearest nucleus which is inside the surface) and  $d_e$  (the distance from the nucleus to the nearest nucleus which is outside the surface). The strong, the weak and no intermolecular interactions are represented in the red, blue and white region, respectively (Figs. 7-9a). The shape index reveals the

hollows and the humps of the crystal, which are represented by the red regions and the blue regions, respectively (Figs. 7-9b). The green area and the blue line were shown in the curvedness (Figs. 7-9c). Herein, we discuss the varieties of the intermolecular interactions in compounds **1-3** based on different position of the hydroxyl groups bonded to the aromatic rings (Table 6).

In compound **1**, the strong hydrogen bonds are C-H···O hydrogen as deep red spot (Fig. 7). Intermolecular contacts are exhibited by finger print plots shown in Fig. 11a. The interactions of O···H/H···O with the contribution of 8.8% can be found. A spur in lower left region represents the contact of H···H (38.4%) interactions. Strong interactions in crystal **1** are C···H/H···C and N···H/H···N with the contribution of 31.4% and 14.5%, respectively. The interactions of C···C can be found to be 2.4%. Specially, the two blunt spikes display the C···H/H···C interconnections, and the two sharp nails reveal the N···H/H···N interactions (Fig. 10a).

When the hydroxyl groups are located in the 3-position of aromatic rings, the strong interactions shown as bright red dots are C-H···O and C-N···H hydrogen bonds (Fig. 8a). The contacts of O···H/H···O can be found to be 11.8%, which is larger than that observed in compound **1**. Compared with crystals **1**, compound **2** has higher the H···H contacts with the contribution of 44.9%. The contribution of 19.6% can be observed for the C···H/H···C contacts. The rest of the contacts interactions are listed as the following: N···H/H···N (11.9%) and C···C (3.8%) (Fig. 10b).

When the hydroxyl groups can be bonded to the *para*-position of the phenyl rings, the red spots reveal the strong N-H···O and O-H···N intermolecular hydrogen bonds (Fig. 9a). As shown in Fig. 10c, among all interactions the H···H interactions give the maximal contribution of 33.2%. The contacts of O···H/H···O can be found to be 14.4%, which is higher than those observed in compounds **1** and **2**. The other intermolecular contacts to the surface are shown as the followings: H···C/C···H

(29.1%), H…N/N…H (16.0%) and C…C (2.3%). The overall contributions of intermolecular interactions to the crystal are illustrated in Fig. 10c.

Notably, the O···H/H···O close contacts exhibit the increasing order from compound 1 to 3: 1<2<3, where the same order can be observed for the total dihedral angles between the phenyl and triazole-yl rings (Table 5). As mentioned above, there exist an order of the luminescent maximal peaks for compounds 1-3 (1>2>3). Obviously, the maximal peaks decrease with the growth of the O···H/H···O close contacts and the dihedral angles, and with the reduction of the hydroxylic steric effects. The observed results can be quantitatively responsible for the luminescent behaviors.

### 4. Conclusion

In summary, we have successfully prepared a set of 4H-amino-1,2,4-triazole derivatives with different hydroxylic positions under the solvothermal reaction conditions. The title compounds are characterized by EA, IR, and powder/single-crystal X-ray diffraction. Notably, it happens the interesting feature with both *trans*- and *cis*-conformation for compound **3**. The photoluminescent properties can be tuned through the position of the substituent groups, but also the luminescent peaks decline down the diminution of the hydroxyl steric effects. The observed results can be further confirmed by the Hirshfeld surface analyses and the dihedral angles between the phenyl and triazole-yl rings. The present strategies based on the design and development of the molecular engineering open an avenue to explore the promising photoluminescent materials. Furthermore, the investigation of compounds based on 4-amino-4*H*-1,2,4-triazole group with the controlled fluorescent behaviors are under the way in our laboratory.

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Appendix A. Supplementary data

CCDC 2067931-2067933 contains the supplementary crystallographic data for compounds **1-3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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A set of x,x'-(4-amino-4*H*-1,2,4-triazole-3,5-diyl) diphenol [x=2 (1), x=3 (2), x=4 (3)], were prepared, which have been characterized by IR, element analysis (EA), single crystal X-ray diffraction, and powder X-ray diffraction (PXRD). Hydrogen bonds (C/N/O–H···O/N) and C-H··· $\pi$  can be clearly observed in these compounds. It surprisedly occurs the presence of *trans*- and *cis*-conformation for compounds **3**. The increasing order of the dihedral angles between the phenyl and triazole-yl rings is 1<2<3. The solid-state luminescent spectra of 1-3 show that the emission maxima are observed at 461, 414 and 402 nm, respectively, which shows the declining order of 1>2>3. The luminescent maximal peaks decrease with the diminution of hydroxylic steric effects. The Hirsfeld surface analyses reveal that the contribution order of the O···H/H···O contacts is 1<2<3, which is in good agreement with that of the dihedral angles, and an inverse proportional to the fluorescent maxima of compounds 1-3.

Compound reference	1	2	3
Chemical formula	$C_{14}H_{12}N_4O_2$	$C_{31}H_{36}N_8O_7$	$C_{14}H_{12}N_4O_2$
Formula Mass	268.28	632.68	268.28
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
<i>a</i> /Å	8.2534(3)	11.4472(4)	9.436(2)
<i>b</i> /Å	9.3891(3)	11.5244(4)	7.5468(19)
c/Å	15.4850(5)	22.5678(10)	18.151(5)
$\alpha/^{\circ}$	90	90	90
$eta/^{\circ}$	90	90	101.976(8)
$\gamma^{\prime \circ}$	90	90	90
Unit cell volume/Å <sup>3</sup>	1199.96(6)	2977.2(2)	1264.5(6)
Temperature/K	100.01(10)	99.98(11)	100(2)
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	$P2_{1}2_{1}2_{1}$	$P2_{1}/n$
No. of formula units per	4	4	4
unit cell, Z			
Radiation type	Μο Κα	Μο Κα	Μο Κα
Absorption coefficient,	0.104	0.103	0.099
$\mu/\mathrm{mm}^{-1}$			
No. of reflections measure	d7106	20206	10203
No. of independent	2652	7044	2881
reflections			

Table 1. Crystal data and structure refinement parameters for compounds 1-3.

	121	12	$\mathbf{re}$ .	-111	$\mathbf{r}$	$\sim$	

R <sub>int</sub>	0.0305	0.0485	0.0787		
Final $R_I$ values $(I > 2\sigma(I))$	0.0358	0.0506	0.0685		
Final $wR(F^2)$ values ( $I >$	0.0797	0.1137	0.1824		
$2\sigma(I))$					
Final $R_i$ values (all data)	0.0394	0.0799	0.0989		
Final $wR(F^2)$ values (all	0.0817	0.1276	0.1991		
data)					
Goodness of fit on $F^2$	1.052	1.075	1.069		
Flack parameters	0.2(7)	-0.6(7)			
CCDC number	2067931	2067932	2067933		
${}^{a}R_{1} = \sum   F_{o}   +  $	$F_{\rm c}  /\Sigma F_{\rm o} $ . <sup>b</sup> wR <sub>2</sub>	$p = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2 - F$	$w(F_0^2)^2]]^{1/2}.$		

Bond lengths/bond angles	Bond lengths	(Å)/BondBond lengths/bond angles	Bond	lengths	(Å)/Bond
	angles (°)		angles	(°)	
1					
01-C1	1.369(2)	O2-C14	1.362(3	3)	
N1-N2	1.386(2)	N1-C7	1.318(3	3)	
N2-C8	1.325(3)	N3-N4	1.416(2	2)	
N3-C7	1.364(3)	N3-C8	1.364(3	3)	
C1-C2	1.403(3)	C1-C6	1.387(3	3)	
C2-C3	1.397(3)	C2-C7	1.473(3	3)	
C3-C4	1.388(3)	C4-C5	1.390(3	3)	
C5-C6	1.392(3)	C8-C9	1.471(3	3)	
C9-C10	1.401(3)	C9-C14	1.414(4	4)	
C10-C11	1.381(3)	C11-C12	1.392(4	4)	
C12-C13	1.381(3)	C13-C14	1.392(3	3)	
N2-N1-C7	107.14(16)	N1-N2-C8	108.17	(17)	
N4-N3-C7	126.15(17)	N4-N3-C8	126.68	(17)	
C7-N3-C8	106.66(17)	O1-C1-C2	117.86	(19)	
01-C1-C6	121.88(18)	C2-C1-C6	120.25	(18)	
C1-C2-C3	119.14(18)	C1-C2-C7	120.84	(17)	

Table 2. Selected bond lengths (Å) and angles (°) for complexes 1-3.

C3-C2-C7	119.64(17)	C2-C3-C4	120.77(18)
C3-C4-C5	119.33(18)	C4-C5-C6	120.8(2)
C1-C6-C5	119.7(2)	N1-C7-N3	109.49(19)
N1-C7-C2	125.34(18)	N3-C7-C2	125.09(19)
N2-C8-N3	108.48(18)	N2-C8-C9	122.8(2)
N3-C8-C9	128.31(19)	C8-C9-C10	122.7(2)
C8-C9-C14	118.83(19)	C10-C9-C14	118.23(19)
C9-C10-C11	121.1(2)	C10-C11-C12	120.1(2)
C11-C12-C13	119.8(2)	C12-C13-C14	120.8(2)
O2-C14-C9	123.40(18)	O2-C14-C13	116.7(2)
C9-C14-C13	119.91(19)		
2			

## 2

O1-C1	1.354(4)	O2-C11	1.360(4)
N1-N2	1.386(4)	N1-C7	1.321(4)
N2-C8	1.317(4)	N3-N4	1.418(3)
N3-C7	1.359(4)	N3-C8	1.378(4)
C1-C2	1.394(5)	C1-C6	1.389(5)
C2-C3	1.391(5)	C3-C4	1.378(5)
C4-C5	1.397(5)	C5-C6	1.390(5)
C5-C7	1.469(5)	C8-C9	1.473(5)
C9-C10	1.395(4)	C9-C14	1.394(5)
C10-C11	1.375(5)	C11-C12	1.395(5)

C12-C13	1.386(5)	C13-C14	1.388(5)
O3-C15	1.370(3)	O4-C27	1.364(4)
N5-N6	1.386(4)	N5-C21	1.320(4)
N6-C22	1.316(4)	N7-N8	1.411(3)
N7-C21	1.375(4)	N7-C22	1.368(4)
C15-C16	1.394(5)	C15-C20	1.386(5)
C16-C17	1.390(5)	C17-C18	1.382(5)
C18-C19	1.396(5)	C19-C20	1.394(5)
C19-C21	1.463(5)	C22-C23	1.465(5)
C23-C24	1.409(5)	C23-C28	1.395(5)
C24-C25	1.376(5)	C25-C26	1.388(5)
C26-C27	1.394(5)	C27-C28	1.381(5)
O5-C29	1.421(4)	O6-C30	1.433(4)
O7-C31	1.424(4)		
N2-N1-C7	108.5(3)	N1-N2-C8	106.9(2)
N4-N3-C7	124.3(3)	N4-N3-C8	129.0(3)
C7-N3-C8	106.2(3)	O1-C1-C2	122.1(3)
O1-C1-C6	117.8(3)	C2-C1-C6	120.1(3)
C1-C2-C3	119.2(3)	C2-C3-C4	121.1(3)
C3-C4-C5	119.5(3)	C4-C5-C6	120.0(3)
C4-C5-C7	121.7(3)	C6-C5-C7	118.2(3)

C1-C6-C5	120.1(3)	N1-C7-N3	108.9(3)
N1-C7-C5	124.3(3)	N3-C7-C5	126.7(3)
N2-C8-N3	109.5(3)	N2-C8-C9	125.7(3)
N3-C8-C9	124.8(3)	C8-C9-C10	121.4(3)
C8-C9-C14	119.1(3)	C10-C9-C14	119.5(3)
C9-C10-C11	120.9(3)	O2-C11-C10	122.2(3)
O2-C11-C12	118.0(3)	C10-C11-C12	119.8(3)
C11-C12-C13	119.4(3)	C12-C13-C14	121.1(3)
C9-C14-C13	119.3(3)	N6-N5-C21	106.7(2)
N5-N6-C22	109.2(3)	N8-N7-C21	125.0(3)
N8-N7-C22	127.7(3)	C21-N7-C22	106.5(2)
O3-C15-C16	117.4(3)	O3-C15-C20	121.8(3)
C16-C15-C20	120.8(3)	C15-C16-C17	118.8(3)
C16-C17-C18	121.2(3)	C17-C18-C19	119.5(3)
C18-C19-C20	120.0(3)	C18-C19-C21	117.7(3)
C20-C19-C21	122.3(3)	C15-C20-C19	119.7(3)
N5-C21-N7	109.4(3)	N5-C21-C19	124.1(3)
N7-C21-C19	126.5(2)	N6-C22-N7	108.2(3)
N6-C22-C23	124.0(3)	N7-C22-C23	127.8(3)
C22-C23-C24	117.9(3)	C22-C23-C28	122.8(3)
C24-C23-C28	119.3(3)	C23-C24-C25	119.7(3)
C24-C25-C26	121.2(3)	C25-C26-C27	118.9(3)

O4-C27-C26	121.6(3)	O4-C27-C28	117.6(3)
C26-C27-C28	120.8(3)	C23-C28-C27	120.0(3)
3			
O1-C1	1.357(3)	O2-C12	1.354(3)
N1-N2	1.382(3)	N1-C7	1.313(3)
N2-C8	1.313(3)	N3-N4	1.405(3)
N3-C7	1.373(3)	N3-C8	1.366(3)
C1-C2	1.388(4)	C1-C6	1.388(4)
C2-C3	1.374(4)	C3-C4	1.396(4)
C4-C5	1.387(3)	C4-C7	1.461(4)
C5-C6	1.379(4)	C8-C9	1.464(4)
C9-C10	1.394(4)	C9-C14	1.392(4)
C10-C11	1.372(4)	C11-C12	1.393(4)
C12-C13	1.391(3)	C13-C14	1.382(4)
N2-N1-C7	108.26(19)	N1-N2-C8	107.8(2)
N4-N3-C7	123.6(2)	N4-N3-C8	129.1(2)
C7-N3-C8	106.5(2)	01-C1-C2	122.2(2)
O1-C1-C6	118.2(2)	C2-C1-C6	119.6(3)
C1-C2-C3	120.1(3)	C2-C3-C4	120.8(3)
C3-C4-C5	118.5(3)	C3-C4-C7	122.1(2)
C5-C4-C7	119.4(2)	C4-C5-C6	121.0(2)

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C1-C6-C5	119.9(2)	N1-C7-N3	108.5(2)
N1-C7-C4	125.9(2)	N3-C7-C4	125.6(2)
N2-C8-N3	109.0(2)	N2-C8-C9	126.8(3)
N3-C8-C9	124.2(2)	C8-C9-C10	121.9(2)
C8-C9-C14	119.4(2)	C10-C9-C14	118.7(2)
C9-C10-C11	120.4(3)	C10-C11-C12	120.5(2)
O2-C12-C11	121.2(2)	O2-C12-C13	119.0(2)
C11-C12-C13	119.8(2)	C12-C13-C14	119.3(2)
C9-C14-C13	121.3(2)		

Compounds	$D-H\cdots A^{a}$	H···A (Å)	D····A (Å)	D–H····A (°)
1	O1-H1···N1 <sup>a</sup>	1.90	2.703(2)	158
	O2-H2…N2	1.86	2.604(2)	147
	N4-H4A····O2 <sup><math>b</math></sup>	2.50	3.135(2)	129
	N4-H4B…O1	2.17	2.837(2)	131
	C10-H10N4	2.35	3.021(3)	128
2	$O2-H\cdots N1^a$	1.92	2.763(3)	174
	О1-На…О5	1.83	2.658(4)	168
	Об-НЬ…ОЗ	1.91	2.733(3)	167
	O3-H3…N6 <sup>b</sup>	1.83	2.662(3)	172
	О5-Нс…Об <sup>b</sup>	1.95	2.789(3)	179
	O4-H4····O7	1.83	2.640(4)	161
	$O7-Hd\cdots O6^{c}$	2.08(4)	2.798(3)	153.9(8)
	N4-He···N2 <sup><math>a</math></sup>	2.464(18)	3.380(3)	166.0(11)
	N4-Hf…O4	2.296(19)	3.042(4)	151.9(5)
	C4-Hl····N4	2.49	3.015(5)	115

Table 3. Hydrogen bond geometries in the crystal structure of compounds 1-3, respectively.

		urnal Pre-proof		
	$C_{12}$ $U_{12}$ $O_{1d}$	2.52	2 272(4)	126
	C18-H18O1	2.53	3.273(4)	136
	$C30-Hs\cdots O2^{e}$	2.58	3.392(5)	140
	C20-H20N8	2.62	3.096(5)	112
	C20-H20····N5 <sup>b</sup>	2.54	3.432(4)	157
3	$O1-H1\cdots N2^{a}$	1.99	2.794(3)	161
	$O2-H2\cdots N1^b$	2.00	2.833(3)	174
	$O2-H2\cdots N2^b$	2.60	3.302(3)	142
	N4-H4A $\cdots$ O2 <sup><math>c</math></sup>	2.39	3.267(3)	170
	N4-H4B $\cdots$ O1 <sup>d</sup>	2.46	3.245(3)	149

Symmetry codes: <sup>*a*</sup>-x,1/2+y,-1/2-z; <sup>*b*</sup>1+x,y,z for 1. <sup>*a*</sup>1/2+x,3/2-y,1-z; <sup>*b*</sup>-1/2+x,1/2-y,1-z; <sup>*c*</sup>1/2-x,1-y,-1/2+z; <sup>*d*</sup>1+x,y,z; <sup>*e*</sup>1/2-x,1-y,1/2+z for 2. <sup>*a*</sup>-1+x,y,z; <sup>*b*</sup>1/2+x,3/2-y,1/2+z; <sup>*c*</sup>2-x,1-y,1-z; <sup>*d*</sup>1/2-x,1/2+y,1/2-z for 3.

Compounds	Cg <sup></sup> Cg	$\pi^{\cdot\cdot\cdot}\pi$ (Å)	C–H <sup>…</sup> Cg	C–H <sup></sup> $\pi$ (Å)
1			C3-H3 <sup></sup> Cg3 <sup>a</sup>	3.374(2)
			C4-H4···Cg1 <sup><math>b</math></sup>	3.563(2)
			C12-H12···Cg2 <sup><math>c</math></sup>	3.480(2)
2	$Cg1 \cdots Cg6^d$	3.506(2)	C31-Ho <sup></sup> Cg5 <sup>c</sup>	3.739(4)
	$Cg2\cdots Cg4^{b}$	3.594(2)	C29-Hw <sup></sup> Cg2 <sup>f</sup>	3.355(4)
	$Cg4\cdots Cg2^{e}$	3.594(2)		
	$Cg6\cdots Cg1^a$	3.506(2)		
3			C3-H3 <sup></sup> Cg2 <sup>a</sup>	3.573(3)
			C5-H5 <sup></sup> Cg3 <sup>b</sup>	3.302(3)
Symmetry co	odes: $a_{1/2+x,-3/2}$	2-y,-z; <sup>b</sup> -x,-1/	/2+y,-1/2-z; <sup>c</sup> -1/2-x	x,-1-y,1/2+z for <b>1</b> .
<sup><i>a</i></sup> 1/2+x,3/2-y,1-	-z; $b-1/2+x,1/2$	/2-y,1-z;	<sup>2</sup> 1/2-x,1-y,-1/2+z;	<sup><i>d</i></sup> -1/2+x,3/2-y,1-z;
<sup>e</sup> 1/2+x,1/2-y,1-	-z; <sup>f</sup> -x,-1/2+y,3/2-2	z for <b>2</b> . <i><sup><i>a</i></sup>1/2-x,</i>	1/2+y,1/2-z; <sup><i>b</i></sup> 3/2-x,	-1/2+y,1/2-z for <b>3.</b>
Cg1=N1-N2-C	28-N3-C7;		Cg2=C	1-C2-C3-C4-C5-C6;
Cg3=C9-C10-0	C11-C12-C13-C1	4 for	<b>1</b> . Cg1	=N1-N2-C8-N3-C7;
Cg2=C1-C2-C	3-C4-C5-C6;		Cg3=C9-C10	-C11-C12-C13-C14;
Cg4=N5-N6-C	222-N7-C21;	Cg5=C15	-C16-C17-C18-C19	D-C20; Cg6=
C23-C24-C25-	·C26-C27-C28	for	<b>2</b> . Cg2=C	1-C2-C3-C4-C5-C6;
Cg3=C9-C10-0	C11-C12-C13-C1	4 for <b>3</b> .		

Table 4. $\pi^{\dots}\pi$ and C–H <sup><math>\dots</math></sup> $\pi$	geometries in the	crystal structure of	compounds 1-3.

	1	2		3
Dihedral Angles (°)	13.0(1), 50.2(1)	28.5(1), 36	6.5(1),	38.3(1), 41.3(1)
		28.4(1), 36.7(	(1)	
Total Angles (°)	63.3	65.0		79.6
Stacking Distances	4.4313(12)	3.506(2)		3.8222(18)
Luminescent Peaks	461	414		402
		~	0	

Table 5 The related parameters of compounds 1-3

Table 6 The close contacts of compounds 1-3

	1	2	3
Н…Н (%)	38.4	44.9	33.2
H…C/C…H (%)	31.4	19.6	29.1
H…N/N…H(%)	14.5	11.9	16.0
O…H/H…O(%)	8.8	11.8	14.4
C…C (%)	2.4	3.8	2.3



Scheme 1 The organic structures.



(b)



Fig. 1. (a) A perspective view of 1. (b) A supramolecular 1D chain through the weak hydrogen bonds

along the *b* axis. (c) A supramolecular 2D network by hydrogen bonds interactions along the crystallographic bc plane in **1**. (d) A stacking diagram of **1** along the *a* axis.



(b)



(c)



Fig. 2. (a) A perspective view of 2. (b) A supramolecular 1D chain through the weak hydrogen bonds along the *b* axis. (c) A supramolecular 2D network by hydrogen bonds interactions along the crystallographic *bc* plane in 2. (d) A stacking diagram of 2 along the *a* axis.







Fig. 3. (a) A perspective view of 3. (b) A supramolecular 1D chain through the weak hydrogen. (c) A supramolecular 2D network by hydrogen bonds interactions along the crystallographic *ac* plane in 3.
(d) A stacking diagram of 3 along the *a* axis.





Fig. 4 IR spectra of compounds 1-3.



Fig. 5 The TGA curves for compounds 1-3.



Fig. 6 The solid-state photoluminescent spectra of compounds 1-3 at room temperature.



Fig. 7 Hirshfeld surface mapped with  $d_{norm}$  (a), shape index (b) and curvedness (c) of compound 1



Fig. 8 Hirshfeld surface mapped with  $d_{norm}$  (a), shape index (b) and curvedness (c) of compound 2



Fig. 9 Hirshfeld surface mapped with  $d_{norm}$  (a), shape index (b) and curvedness (c) of compound 3



Fig. 10 Finger print plots of compounds 1-3 (a-c, respectively)

### Highlights

- A set of 4-amino-4H-1,2,4-triazole have been synthesized
- Their crystal state structures were characterized by single crystal X-ray diffraction.
- The luminescent properties can be controlled by the hydroxylic position.
- The emission maxima are proportional to the O···H/H···O interactions.
- The emission bands are inverse proportional to the dihedral angles.

### **Declaration of interests**

 $\Box$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

There are no conflicts to declare.