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Synthesis of Novel *N,N′,N″*-Tris[aryl(hetaryl)-methylideneamino]guanidine Derivatives as Efficient and Selective Colorimetric Sensors for Fluoride Ion

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Abstract—A series of *N,N′,N″*-tris[aryl(hetaryl)methylideneamino]guanidines have been synthesized in good yields by condensation of *N,N′,N″*-triaminoguanidine hydrochloride with aromatic and heteroaromatic aldehydes. All compounds have been characterized by ^{1}H and ^{13}C NMR and FT-IR spectra, and the molecular structure of one compound has been determined by single crystal X-ray diffraction. Study of the optical properties of the title compounds in the presence of fluoride ions has shown selective color change from colorless to yellow and purple due to red shift in their UV-Vis absorption spectra.

Keywords: *N,N′,N″*-Triaminoguanidinium chloride, Schiff bases, selective chemosensor, X-ray analysis.

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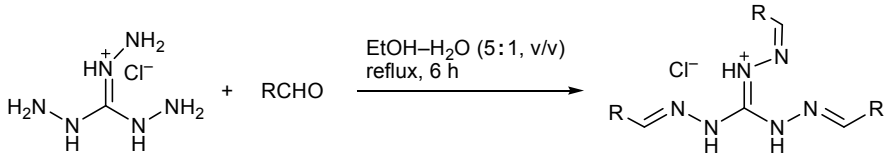
Being nitrogen-rich compounds, *N,N′,N″*-triaminoguanidine derivatives have broad ranges of physical, chemical, and biological properties and found wide applications in fuels, enzyme inhibitors, medicines, and chemical engineering fields [1, 2]. In particular, Schiff bases derived from triaminoguanidine are widely used as multidentate organic ligands to prepare various polynuclear transition metal complexes [3–9]. In most studies reported so far, triaminoguanidine easily reacted with typical carbonyl compounds; for example, reactions of triaminoguanidinium salts with aldehydes, ketones, 1,3-diketones, acyl chlorides, carboxylic acids, sodium nitrite, and cyanogen bromide have been described [10–18]. Among products of these reactions, *N,N′,N″*-tris(arylmethylideneamino)- and *N,N′,N″*-tris(alkylideneamino)guanidinium salts possess an attractive C_3-symmetrical molecular platform, which could act as triangular ligand to form transition metal complexes with novel architectures [3–9]. It is well known that guanidinium moieties are widely used as anion binding sites in colorimetric molecular probes selective for fluoride ion [19–22]. We previously reported a series of diaminoguanidinium chloride derivatives as efficient and selective colorimetric sensors for fluoride ion [23]. Herein, we describe the synthesis of a series of new tris[aryl-(hetaryl)methylideneamino]guanidinium chlorides as efficient and selective colorimetric sensors for fluoride ion via naked eye detection. In addition, their ultraviolet spectra in the presence of fluoride ions are also reported.

The desired *N,N′,N″*-tris[aryl(hetaryl)methylideneamino]guanidinium chlorides **3a**–**3u** were easily prepared in moderate to good yields by condensation of *N,N′,N″*-triaminoguanidine hydrochloride (**1**) with the corresponding aromatic and heteroaromatic aldehydes **2a**–**2u** (Scheme 1). The ^{1}H NMR spectra of **3a**–**3u** showed a broadened singlet in the region δ 11.13–12.54 ppm due to the NH proton, and the signal at δ 8.31–9.22 ppm was assigned to the azomethine proton (CH=N). In the ^{13}C NMR spectra of **3a**–**3u**, the signal around δ_C 160 ppm was attributed to the CH=N carbon, which agreed well with the data for tris(propan-2-ylideneamino)guanidine [12]. The IR spectra of **3a**–**3u** contained a broadened absorption band in the region 3400–3200 cm^{-1} due to N–H stretching vibrations, and in the region 1700–1600 cm^{-1} due to C=N stretchings, which is consistent with the data for structurally related triaminoguanidine derivatives [12].

The structure of **3u**·H_2O was established by single-crystal X-ray diffraction. Figure 1 shows the molecular structure of **3u**·H_2O and its crystal packing. All carbon and nitrogen atoms in the cationic moiety of **3u** have sp^2 hybridization, and the bonds between the central

Scheme 1.



R = 2-HOC$_6$H$_4$ (**a**), 2-HO-5-ClC$_6$H$_3$ (**b**), 2-HO-5-O$_2$NC$_6$H$_3$ (**c**), 2-HO-3,5-Br$_2$C$_6$H$_2$ (**d**), 2-HO-4-Et$_2$NC$_6$H$_4$ (**e**), 2-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$ (**f**), 4-*i*-PrC$_6$H$_4$ (**g**), 2-O$_2$NC$_6$H$_4$ (**h**), 3-HOC$_6$H$_4$ (**i**), 3-HO-4-MeOC$_6$H$_3$ (**j**), 4-MeSO$_2$C$_6$H$_4$ (**k**), 4-Me$_2$NC$_6$H$_4$ (**l**), 4-MeOC$_6$H$_4$ (**m**), 4-BrC$_6$H$_4$ (**n**), Ph (**o**), (*E*)-PhCH=CH (**p**), naphthalen-1-yl (**q**), pyridin-3-yl (**r**), thiophen-2-yl (**s**), thiophen-3-yl (**t**), 5-bromothiophen-2-yl (**u**).

carbon and nitrogen atoms have a partial double-bond character. The average C=N bond length is 1.266(10) Å, which is significantly shorter than the average C–N bond length [1.330(9) Å]. This is in good agreement with the data for tris(5-bromo-2-hydroxybenzylideneamino)guanidinium chloride (C=N 1.279(5) Å, C–N 1.327(7) Å) [7, 24]. The planar structure of the N_2CN entity follows from the sum of the angles subtended at the central carbon atom, which equals 359.9(7)°. As expected, N–H···Cl, C–H···Cl, and O–H···Cl hydrogen bonding interactions exist in the crystal structure of **3u** · H_2O, as shown in Fig. 1b.

The colorimetric changes and absorption and emission spectra of compounds **3a**–**3u** were recorded from 1.0×10^{-4} M solutions in acetonitrile. Initially, colorimetric changes of **3a** in the presence of different halide ions (F^-, Cl^-, Br^-) were tested. Only in the presence of fluoride ions, solutions of **3a** changed from colorless to yellow, indicating that **3a** could detect fluoride ion selectively. Then, colorimetric changes of **3b**–**3u** in the presence of fluoride ion were examined (Fig. 2), and distinct color changes for most of these compounds were observed in the presence of fluoride ions. Exceptions were compounds **3g**, **3i**, **3l**, and **3m** which bear electron-donating substituents. Fluoride ions caused drastic color changes from colorless to yellow and even to red, reddish orange, and purple. Compounds **3b**–**3d**, **3h**, **3k**, **3n**, and **3u** containing electron-withdrawing groups like nitro, bromo, chloro, or methanesulfonyl on the phenyl ring or heterocycle, showed remarkable color changes, presumably due to the presence of a positive charge on the central nitrogen atom of the trisaminoguanidinium moiety, which favored selective electrostatic interaction with spherical and basic fluoride ions [23]. If there are electron-withdrawing groups in the Schiff base moieties, the positive charge on the central nitrogen is higher, so that the interaction with fluoride ion is enhanced.

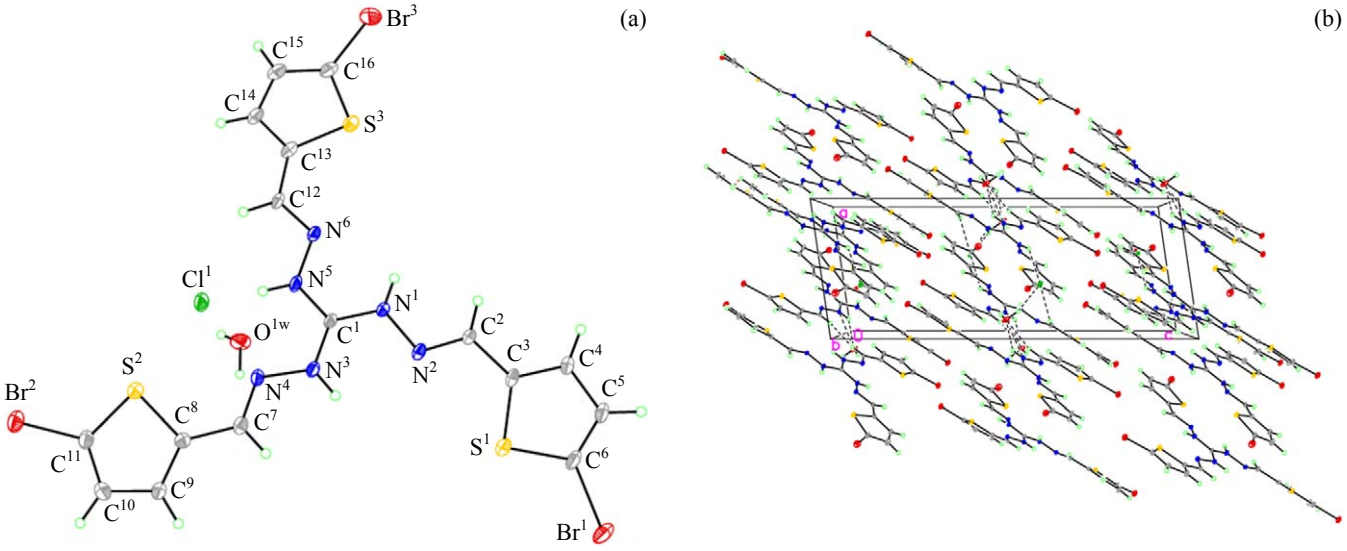


Fig. 1. (a) Structure of the molecule of *N,N′,N″*-tris[(5-bromothiophen-2-yl)methylideneamino]guanidine hydrochloride (**3u**) hydrate according to the X-ray diffraction data with arbitrary atom numbering. Non-hydrogen atoms are shown as thermal displacement ellipsoids with a probability of 40%; (b) packing of molecules **3u** · H_2O in a unit cell viewed along the crystallographic *ac* plane; hydrogen bonds are shown as dashed lines.

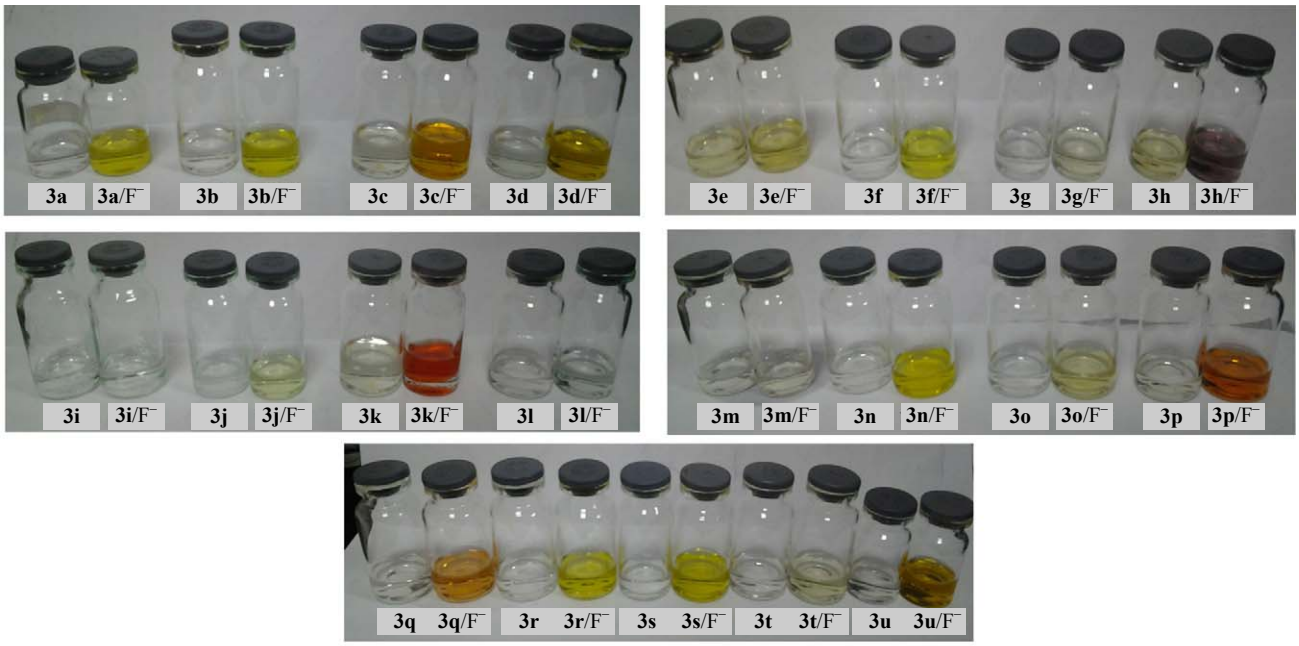


Fig. 2. Color change of compounds **3a**–**3u** in acetonitrile in the presence of fluoride anion.

The UV-Vis spectral properties of **3a**–**3u** were studied in the presence of tetrabutylammonium fluoride (TBAF), and the corresponding changes in the optical spectra are shown in Fig. 3. The UV-Vis absorption peak at λ 359 nm of **3a** was mainly due to the Ar–CH=N–NH conjugated bond system [25]. In the presence of fluoride anion, the intensity of that peak decreases, and a new absorption band appears in the region λ 400–600 nm (Fig. 3). For compounds **3g**, **3l**, and **3m** bearing electron-donating groups like isopropyl, dimethylamino, and methoxy, the position of the UV-Vis absorption maximum almost did not change, but the absorbance decreased. By contrast, for compounds **3a**–**3f**, **3i**–**3k**, and **3n**–**3u** bearing electron-withdrawing or auxochromic moieties like hydroxy, chloro, bromo, nitro, or methanesulfonyl, the UV-Vis absorption maximum shifted red in the presence of fluoride ions (Fig. 3), which might enhance the interaction of trisaminoguanidinium moiety with fluoride ion. These findings were consistent with the results of colorimetric change testing, according to which compounds **3b**–**3d**, **3f**, **3k**, **3n**, and **3u** showed more appreciable color changes than **3g**, **3i**, **3l**, and **3m** (Fig. 2).

In summary, we have synthesized a series of new triaminoguanidinium chloride derivatives functionalized with three Schiff base moieties. Single crystal X-ray crystallography on one typical compound has confirmed its ionic form. The colorimetric and UV-Vis spectral studies in acetonitrile solution revealed that *N,N′,N″*-tris[aryl(hetaryl)methylideneamino]guanidinium chlorides with electron-withdrawing groups exhibited selective color changes in the presence of fluoride ions and appreciable red shift in their UV-Vis absorption spectra.

EXPERIMENTAL

N,N′,N″-Triaminoguanidine hydrochloride was supplied from Ma'anshan Huanyu Chemical Co. Tetrabutylammonium fluoride/bromide/chloride and aromatic and heteroaromatic aldehydes were purchased from Alfa Aesar, Sigma-Aldrich, J&K®, Aladdin®, Energy Chemical, and Sinopharm Chemical Reagent Co. All solvents were purified by routine procedures and distilled under dry nitrogen before use. Unless otherwise specified, all analytical reagents (>99.5% purity) were purchased from Adamas-beta® and were used as received without further purification. Melting points were determined in capillaries using an X4 digital melting point apparatus and are uncorrected. The IR spectra were recorded on a Nicolet 6700 spectrophotometer from pressed KBr discs. The UV absorption spectra were recorded on a Shimadzu UV-2501 PC spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance AV 400 spectrometer at 400 and 100 MHz, respectively, in DMSO-d_6 or $CDCl_3$ with tetramethylsilane as internal standard.

Typical procedure for the preparation of *N,N′,N″*-tris[aryl(hetaryl)methylideneamino]guani-

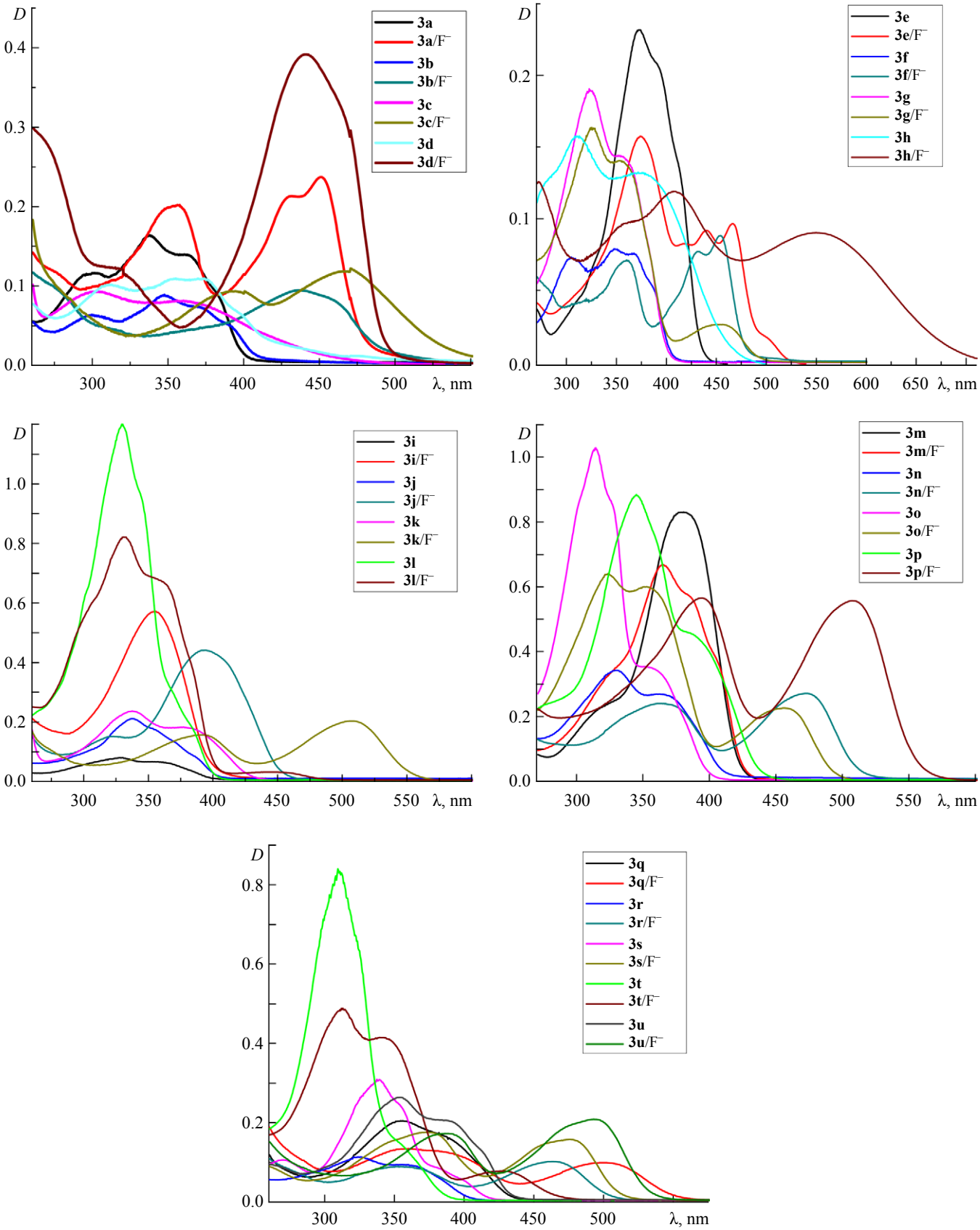


Fig. 3. Changes in the UV-Vis absorption spectra of compounds **3a**–**3u** in the presence of fluoride ions.

dinium chlorides 3a–3u. A solution of 7.5 mmol of aldehyde **2a**–**2u** in 10 mL of ethanol was added dropwise to a mixture of *N*,*N*′,*N*″-triaminoguanidine hydrochloride (0.351 g, 2.5 mmol) and 48 mL of ethanol–water (5:1 by volume). The mixture was refluxed with stirring for 6 h and cooled to room temperature, and the white or yellow precipitate was filtered off, washed with water, ethanol, and diethyl ether and dried under reduced pressure.

***N,N′,N″*-Tris(2-hydroxybenzylideneamino)guanidine hydrochloride (3a).** Yield 0.91 g (80%), white powder, mp 210–213°C. IR spectrum, ν, cm^{-1}: 3240 (NH), 1623 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 11.13 br.s (3H, NH), 9.00 s (3H, OH), 8.75 s (3H, CH=N), 7.69 d (3H, H_{arom}, J = 8.1 Hz), 7.45–7.35 m (3H, H_{arom}), 7.27 t (3H, H_{arom}, J = 7.7 Hz), 6.95 d (3H, H_{arom}, J = 8.9 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 163.17 (CH=N), 159.10 (CH=N), 157.43 (C_{arom}), 133.69 (C_{arom}), 131.22 (C_{arom}), 120.19 (C_{arom}), 120.06 (C_{arom}), 116.63 (C_{arom}).

***N,N′,N″*-Tris(5-chloro-2-hydroxybenzylideneamino)guanidine hydrochloride (3b).** Yield 1.01 g (73%), yellow powder, mp 241–242°C. IR spectrum, ν, cm^{-1}: 3287 (NH), 1652 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.02 br.s (3H, NH), 10.76 s (3H, OH), 8.91 s (3H, CH=N), 8.19 s (3H, H_{arom}), 7.34 d (3H, H_{arom}, J = 6.8 Hz), 7.00 d (3H, H_{arom}, J = 8.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 155.42 (CH=N), 149.72 (CH=N), 146.02 (C_{arom}), 133.14 (C_{arom}), 126.05 (C_{arom}), 123.97 (C_{arom}), 122.86 (C_{arom}), 118.24 (C_{arom}).

***N,N′,N″*-Tris(2-hydroxy-5-nitrobenzylideneamino)guanidine hydrochloride (3c).** Yield 0.64 g (43%), yellow powder, mp 276–279°C. IR spectrum, ν, cm^{-1}: 3404 (OH), 3267 (NH), 1655 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 11.28 br (3H, NH), 9.30 s (3H, OH), 8.92 s (3H, CH=N), 8.42 d (3H, H_{arom}, J = 3.1 Hz), 8.17 d (3H, $H_{arom,}$ J = 9.8 Hz), 7.12 d (3H, $H_{arom,}$ J = 14.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 159.57 (CH=N), 144.29 (CH=N), 141.14 (C_{arom}), 139.04 (C_{arom}), 128.70 (C_{arom}), 124.17 (C_{arom}), 120.56 (C_{arom}), 115.84 (C_{arom}).

***N,N′,N″*-Tris(3,5-dibromo-2-hydroxybenzylideneamino)guanidine hydrochloride (3d).** Yield 1.17 g (50%), yellow powder, mp 268–271°C. IR spectrum, ν, cm^{-1}: 3339 (NH), 1621 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 11.78 br.s (3H, NH), 8.74 s (3H, OH), 8.51 s (3H, CH=N), 7.84 d (3H, H_{arom}, J = 3.9 Hz), 7.68 d (3H, H_{arom}, J = 3.9 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 156.36 (CH=N), 146.54 (CH=N), 140.50 (C_{arom}), 135.91 (C_{arom}), 132.70 (C_{arom}), 120.15 (C_{arom}), 114.59 (C_{arom}), 113.37 (C_{arom}).

Table 1. Crystallographic data and experimental details for compound **3u**·H_2O

Parameter	Value
Formula	$C_{16}H_{14}N_6OS_3ClBr_3$
Molecular weight	677.69
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	8.5480(15)
b, Å	12.510(2)
c, Å	22.164(4)
β, deg	98.259(3)
V, Å^3	2345.7(7)
Z	4
d_{calc}, g/cm^3	1.919
Temperature, K	296(2)
F(000)	1320
μ(Mo K_α), mm^{-1}	5.562
Total number of reflections	6715
Number of independent reflections	3709
R_{int}	0.0955
Number of variables	277
R_1[a]/wR_2[b] [$I > 2s(I)$]	0.0699/0.1588
R_1[a]/wR_2[b] (all data)	0.1182/0.1769
Goodness of fit S[c]	0.848
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	+0.993/–1.633

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [Sw(F_o^2 - F_c^2)^2/Sw(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.
[c] $S = [Sw(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

***N,N′,N″*-Tris[4-(diethylamino)-2-hydroxybenzylideneamino]guanidine hydrochloride (3e).** Yield 0.88 g (53%), yellow powder, mp 174–176°C. IR spectrum, ν, cm^{-1}: 3461 (NH), 1627 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 11.28 br.s (3H, NH), 9.90 s (3H, OH), 8.64 s (3H, CH=N), 7.75 d (3H, H_{arom}, J = 14.9 Hz), 7.40 d (3H, H_{arom}, J = 2.9 Hz), 6.34–6.21 m (3H, H_{arom}), 3.60–3.49 m (6H, NCH_2), 1.18 t (9H, $CH_2C\mathbf{H}_3$, J = 12.6 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 159.37 (CH=N), 152.36 (CH=N), 144.53 (C_{arom}), 142.78 (C_{arom}), 130.01 (C_{arom}), 109.28 (C_{arom}), 105.12 (C_{arom}), 98.38 (C_{arom}), 45.09 (NCH_2), 12.89 (CH_3).

***N,N′,N″*-Tris(3,5-di-*tert*-butyl-2-hydroxybenzylideneamino)guanidine hydrochloride (3f).** Yield

1.18 g (60%), white powder, mp 244–247°C. IR spectrum, ν, cm^{-1}: 3450 (NH), 1619 (C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 11.76 br.s (3H, NH), 10.51 s (3H, OH), 8.67 s (3H, CH=N), 7.72 d (3H, H_{arom}, J = 14.0 Hz), 7.25–7.19 m (3H, H_{arom}), 1.33 s (27H, *t*-Bu), 1.27 s (27H, *t*-Bu). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 155.38 (CH=N), 142.86 (CH=N), 142.53 (C_{arom}), 140.50 (C_{arom}), 139.71 (C_{arom}), 125.60 (C_{arom}), 123.43 (C_{arom}), 120.89 (C_{arom}), 35.51 [**C**$(CH_3)_3$], 34.76 [**C**$(CH_3)_3$], 12.80 (CH_3).

***N,N′,N″*-Tris[4-(propan-2-yl)benzylideneamino]guanidine hydrochloride (3g).** Yield 1.05 g (79%), white powder, mp 208–211°C. IR spectrum, ν, cm^{-1}: 3033 (NH), 1634 (C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 11.99 br.s (3H, NH), 8.69 s (3H, CH=N), 7.90–7.76 m (6H, H_{arom}), 7.48–7.35 m (6H, H_{arom}), 3.02–2.90 m [3H, $(CH_3)_2$C**H**], 1.24 d (18H, CH_3, J = 6.9 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 152.28 (CH=N), 151.52 (CH=N), 149.38 (C_{arom}), 144.92 (C_{arom}), 144.28 (C_{arom}), 131.35 (C_{arom}), 128.80 (C_{arom}), 127.23 (C_{arom}), 33.95 (CH), 24.11 (CH_3).

***N,N′,N″*-Tris(2-nitrobenzylideneamino)guanidine hydrochloride (3h).** Yield 1.01 g (75%), yellow powder, mp 212–214°C. IR spectrum, ν, cm^{-1}: 3299 (NH), 1635 (C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 11.89 br.s (3H, NH), 8.99 s (3H, CH=N), 7.89–7.74 m (6H, H_{arom}), 7.42–7.12 m (6H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 151.19 (CH=N), 148.83 (CH=N), 145.46 (C_{arom}), 134.12 (C_{arom}), 131.61 (C_{arom}), 129.33 (C_{arom}), 128.53 (C_{arom}), 125.12 (C_{arom}).

***N,N′,N″*-Tris(3-hydroxybenzylideneamino)guanidine hydrochloride (3i).** Yield 0.71 g (63%), white powder, mp 245–248°C. IR spectrum, ν, cm^{-1}: 3266 (NH), 1646 (C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 12.06 br.s (3H, NH), 9.82 s (3H, OH), 8.63 s (3H, CH=N), 7.42–7.29 m (9H, H_{arom}), 7.08–6.95 m (3H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 156.69 (CH=N), 145.32 (CH=N), 142.54 (C_{arom}), 136.44 (C_{arom}), 130.35 (C_{arom}), 120.48 (C_{arom}), 116.76 (C_{arom}), 114.64 (C_{arom}).

***N,N′,N″*-Tris(3-hydroxy-4-methoxybenzylideneamino)guanidine hydrochloride (3j).** Yield 0.96 g (71%), white powder, mp 260–263°C. IR spectrum, ν, cm^{-1}: 3503 (OH), 3056 (NH), 1644 (C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 11.95 br.s (3H, NH), 9.71 s (3H, OH), 8.31 s (3H, CH=N), 7.61–7.53 m (3H, H_{arom}), 7.27–7.18 m (3H, H_{arom}), 6.90–6.82 m (3H, H_{arom}), 3.86 s (9H, OCH_3). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 151.49 (CH=N), 150.39 (CH=N), 148.86 (C_{arom}), 148.52 (C_{arom}), 125.12 (C_{arom}), 123.76 (C_{arom}), 115.85 (C_{arom}), 111.09 (C_{arom}), 46.12 (OCH_3).

***N,N′,N″*-Tris[4-(methanesulfonyl)benzylideneamino)guanidine hydrochloride (3k).** Yield 0.96 g (60%), white powder, mp 213–215°C. IR spectrum, ν, cm^{-1}: 3410 (OH), 3021 (NH), 1638 (C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 11.43 br (3H, NH), 8.77 s (3H, CH=N), 8.20–7.98 m (6H, H_{arom}), 7.85–7.80 m (6H, H_{arom}), 3.28 s (9H, CH_3). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 150.54 (CH=N), 149.23 (CH=N), 144.92 (C_{arom}), 142.51 (C_{arom}), 142.48 (C_{arom}), 138.53 (C_{arom}), 129.10 (C_{arom}), 127.83 (C_{arom}), 43.85 (CH_3).

***N,N′,N″*-Tris[4-(dimethylamino)benzylideneamino]guanidine hydrochloride (3l).** Yield 0.88 g (66%), white powder, mp 213–216°C. IR spectrum, ν, cm^{-1}: 3322 (NH), 1642 (C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 11.59 br.s (3H, NH), 8.54 s (3H, CH=N), 7.76–7.59 m (6H, H_{arom}), 7.09–6.82 m (6H, H_{arom}), 3.01 s (18H, NCH_3). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 152.44 (CH=N), 151.46 (CH=N), 148.30 (C_{arom}), 144.28 (C_{arom}), 142.13 (C_{arom}), 130.07 (C_{arom}), 120.88 (C_{arom}), 111.99 (C_{arom}), 36.47 (NCH_3).

***N,N′,N″*-Tris(4-methoxybenzylideneamino)guanidine hydrochloride (3m).** Yield 0.91 g (74%), white powder, mp 187–189°C. IR spectrum, ν, cm^{-1}: 3396 (OH), 3074 (NH), 1642 (C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 11.92 br.s (3H, NH), 8.65 s (3H, CH=N), 7.93–7.79 m (6H, H_{arom}), 7.18–6.99 m (6H, H_{arom}), 3.84 s (9H, OCH_3). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 162.07 (CH=N), 151.13 (CH=N), 148.52 (C_{arom}), 144.08 (C_{arom}), 142.28 (C_{arom}), 130.41 (C_{arom}), 126.14 (C_{arom}), 114.78 (C_{arom}), 55.91 (OCH_3).

***N,N′,N″*-Tris(4-bromobenzylideneamino)guanidine hydrochloride (3n).** Yield 0.82 g (51%), white powder, mp 219–222°C. IR spectrum, ν, cm^{-1}: 3415 (NH), 1639 (C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 12.28 br.s (3H, NH), 8.72 s (3H, CH=N), 7.95–7.69 m (6H, H_{arom}), 7.54–7.31 m (6H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 167.83 (CH=N), 156.92 (CH=N), 149.28 (C_{arom}), 144.80 (C_{arom}), 141.76 (C_{arom}), 128.93 (C_{arom}), 125.88 (C_{arom}), 113.79 (C_{arom}).

***N,N′,N″*-Tris(benzylideneamino)guanidine hydrochloride (3o).** Yield 0.65 g (64%), white powder, mp 184–186°C. IR spectrum, ν, cm^{-1}: 3388 (NH), 1636 (C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 12.10 br.s (3H, NH), 8.75 s (3H, CH=N), 8.06–7.91 m (6H, H_{arom}), 7.53–7.41 m (9H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 149.02 (CH=N),

144.82 (CH=N), 144.20 (C_{arom}), 133.46 (C_{arom}), 131.83 (C_{arom}), 129.52 (C_{arom}), 128.04 (C_{arom}), 125.27 (C_{arom}).

***N,N′,N″*-Tris[(*E*)-3-phenylprop-2-en-1-ylideneamino]guanidine hydrochloride (3p).** Yield 0.82 g (68%), yellow powder, mp 178–181°C. IR spectrum, ν, cm^{-1}: 3410 (OH), 3026 (NH), 1634 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.18 br.s (3H, NH), 8.46 s (3H, CH=N), 7.68–7.57 m (6H, H_{arom}), 7.48–7.35 m (9H, H_{arom}), 7.24 d (3H, PhC**H**=, J = 16.0 Hz), 7.02 d.d (3H, Ph–CH=C**H**, J = 16.1, 9.3 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 152.98 (CH=N), 148.89 (CH=N), 144.46 (C_{arom}), 142.02 (C_{arom}), 135.92 (C_{arom}), 129.25 (C_{arom}), 129.47 (C_{arom}), 127.78 (C_{arom}), 127.74 (Ph**C**H=), 124.60 (PhCH=**C**H).

***N,N′,N″*-Tris[(naphthalen-1-yl)methylideneamino]guanidine hydrochloride (3q).** Yield 0.97 g (70%), white powder, mp 198–200°C. IR spectrum, ν, cm^{-1}: 3403 (OH), 3047 (NH), 1636 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.34 br.s (3H, NH), 8.70 s (3H, CH=N), 8.55–8.40 m (6H, H_{arom}), 8.26–8.01 m (6H, H_{arom}), 7.79–7.60 m (9H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 149.94 (CH=N), 144.78 (CH=N), 133.85 (C_{arom}), 131.98 (C_{arom}), 131.47 (C_{arom}), 129.47 (C_{arom}), 128.92 (C_{arom}), 128.00 (C_{arom}), 126.87 (C_{arom}), 126.56 (C_{arom}), 126.09 (C_{arom}), 123.12 (C_{arom}).

***N,N′,N″*-Tris[(pyridin-3-yl)methylideneamino]guanidine hydrochloride (3r).** Yield 0.56 g (57%), yellow powder, mp 178–180°C. IR spectrum, ν, cm^{-1}: 3426 (OH), 3048 (NH), 1635 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.54 br.s (3H, NH), 9.22 s (3H, CH=N), 8.85–8.79 m (3H, H_{arom}), 8.74–8.50 m (6H, H_{arom}), 7.66–7.54 m (3H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 149.92 (CH=N), 149.17 (CH=N), 144.41 (C_{arom}), 142.13 (C_{arom}), 136.13 (C_{arom}), 129.74 (C_{arom}), 124.70 (C_{arom}).

***N,N′,N″*-Tris[(thiophen-2-yl)methylideneamino]guanidine hydrochloride (3s).** Yield 0.68 g (64%), yellow powder, mp 188–191°C. IR spectrum, ν, cm^{-1}: 3464 (OH), 3066 (NH), 1633 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.07 br.s (3H, NH), 8.88 s (3H, CH=N), 7.85 d (3H, H_{Th}, J = 5.0 Hz), 7.69 d (3H, H_{Th}, J = 3.6 Hz), 7.25–7.14 m (3H, H_{Th}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 148.65 (CH=N), 146.71 (CH=N), 137.54 (C_{Th}), 133.34 (C_{Th}), 131.47 (C_{Th}), 128.64 (C_{Th}).

***N,N′,N″*-Tris[(thiophen-3-yl)methylideneamino]guanidine hydrochloride (3t).** Yield 0.65 g (62%), yellow powder, mp 195–198°C. IR spectrum, ν, cm^{-1}: 3389 (OH), 3072 (NH), 1642 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.01 br.s (3H, NH), 8.78 s (3H, CH=N), 8.17 d (3H, thiophene, J = 2.7 Hz), 7.91–7.86 m (3H, H_{Th}), 7.75–7.68 m (3H, H_{Th}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 149.27 (CH=N), 146.63 (CH=N), 136.95 (C_{Th}), 131.00 (C_{Th}), 128.16 (C_{Th}), 126.33 (C_{Th}).

***N,N′,N″*-Tris[(5-bromothiophen-2-yl)methylideneamino]guanidine hydrochloride (3u).** Yield 1.02 g (62%), yellow powder, mp 181–183°C. IR spectrum, ν, cm^{-1}: 3313 (OH), 3008 (NH), 1627 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.09 br.s (3H, NH), 8.83 s (3H, CH=N), 7.51 d (3H, H_{Th}, J = 4.0 Hz), 7.36 d (3H, H_{Th}, J = 4.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 148.64 (CH=N), 145.90 (CH=N), 139.36 (C_{Th}), 134.17 (C_{Th}), 132.02 (C_{Th}), 127.54 (C_{Th}).

Single crystals of **3u**·H_2O were grown by recrystallization from ethanol–water (7:3, v/v). The crystallographic data and experimental details of the X-ray diffraction study are summarized in Table 1. Reflection intensities were measured on a Bruker SMART APEX 2 CCD diffractometer (Mo K_α radiation, l 0.71073 Å, graphite monochromator) at 293(2) K. The data were processed using SAINT software [26]. A correction for absorption was applied using SADABS [27]. The structure was solved by the direct method and was refined against F^2 by the full-matrix least-squares method using SHELXTL software package [28, 29]. All non-hydrogen atoms, expect for the solvate molecule, were refined in anisotropic approximation. The positions of all hydrogen atoms were generated geometrically (C_{sp3}–H 0.96, C_{sp2}–H = 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on the respective parent carbon or nitrogen atoms in the final least-squares refinement cycles. The X-ray diffraction data for **3u**·H_2O were deposited to the Cambridge Crystallographic Data Centre (CCDC entry no. 18871067) and are available at *www.ccdc.cam.ac.uk/data_request/cif*.

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CONFLICT OF INTERESTS

The authors declare the absence of conflict of interests.

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