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ORIGINAL RESEARCH

Synthesis, structural analysis, and photophysical properties of bi-1,2,3-triazoles

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Abstract

Structural insights of a group of bi-1,2,3-triazoles derived from oxidative CuAAC are described through an X-ray crystallography study, distinguishing a dihedral angle which is ranged from 76.45 to 86.39° between the two 1,2,3-triazole rings. In addition, compound **1** containing a phenyl moiety displays a strong blue emission ($\lambda_{em} = 394$ nm); this structure-related photoluminescence is attributed to the rigidity of the molecule and the conjugation between phenyl groups and the triazole fragments.

Keywords Bi-1,2,3-triazole · Crystal structure · Dihedral angle · Fluorescent emission

Introduction

5,5′-(1,2,3-Triazolyl)-1,2,3-triazoles, usually known as bi-1,2,3-triazoles, are promising molecules derived from oxidative copper-catalyzed azide-alkyne cycloaddition (CuAAC) [1, 2]. Since their discovery by Angell and Burgess [3], the number of works about the synthesis of bi-1,2,3-triazoles have increased considerably in recent years; however, there are few reports which describe structural and other physical characteristics [4–11].

Bi-1,2,3-triazole structure is similar to other biaryl compounds such as binaphthyls [12–14], bipyridines [15], biimidazoles [16, 17], bipyrazoles [18, 19], and 4,4′-bi-1,2,4-triazoles [20, 21]. This characteristic converts bi-1,2,3-triazoles in potential useful ligands for catalysis with the advantage that these compounds are easily available from oxidative CuAAC reaction. Hence, structural studies in bi-1,2,3-triazoles are important in order to describe properties such as possible coordination sites and stable conformations, especially those which are related to the aromatic rings linked by a single bond forming the biaryl part of the molecule. For example, Zhu and coworkers found rigid axially chiral structures in bi-1,2,3-triazoles with a broader range of dihedral angle distribution than that of BINAPs which provide more opportunities for ligand design in catalysis area [5].

On the other hand, there is a significant current interest in the development of fluorescent triazole derivatives owing to their well-known biological properties that offer promise for medical applications and more recently due to their use as optical molecular sensors for ionic species [22]. Particularly, the emission upon excitation is a physical property that has been found several applications lately in sensing of inorganic anions [23–25], color emitting devices [26], and metal chemosensing characterization of 1,2,3-triazole-based regioisomers [27–29]. The photophysical properties of organic fluorophores are essentially dependent on the conjugated aromatic rings, planarity of the system, solvation environment, and substituent groups in the fluorescent core [22, 30]. In this context, CuAAC reaction has allowed the preparation of a wide variety of triazole-based molecules, from modest push-pull chromophores/fluorophores [31, 32] to multipolar structures with non-linear optical responses such as two-photon absorption [33]. In this regard, the abovementioned photophysical properties have not been already described for bi-1,2,3-triazoles, and only some reported transition metal complexes of bi-1,2,3-triazoles exhibit these characteristics [34–37].

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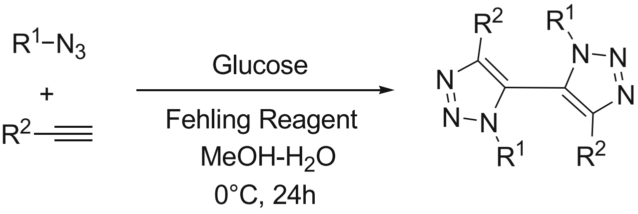
In connection with other projects, we some time ago initiated studies on the synthesis of bi-1,2,3-triazoles, few examples of which were then known, as well as thorough structural and photophysical property studies about this kind of compounds. In light of the new discoveries about this topic, we consider disclosing our most recent results in this area.



Scheme 1 Synthesis of bi-1,2,3-triazoles

Experimental

General

The starting materials were purchased from Aldrich Chemical Co. and were used without further purification. Solvents were distilled before use. The tartrate-NaOH solution (Fehling B solution) was prepared dissolving sodium hydroxide (23.5 g, 0.04 mol) and tartaric acid (18.3 g, 0.012 mol) in H_2O (100 mL). The $CuSO_4$ solution (Fehling A solution) was prepared by dissolving $CuSO_4 \cdot 5H_2O$ (9.89 g, 0.039 mol) in H_2O (100 mL). Silica plates of 0.20-mm thickness were used for thin layer chromatography. Melting points were determined with a Krüss Optronic melting point apparatus and they are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AVANCE 300 or a Varian 500-MHz instrument; the chemical shifts (δ) are given in ppm relative to TMS as internal standard (0.00). For analytical purposes, the mass spectra were recorded on a Shimadzu GCMS-QP2010 Plus in the EI mode, 70 eV, 200 °C via direct inlet probe. Only the molecular and parent ions (*m*/*z*) are reported. IR spectra were recorded on a Bruker TENSOR 27 FT instrument.

The absorption and emission spectra were recorded from methanolic solutions of compounds **1**–**5** (10 μM and 2 μM respectively) in a quartz cuvette placed in a compartment of spectrophotometer thermostated at 25.0° ± 0.1 on a Cary-100 Agilent UV-vis spectrophotometer and Cary Eclipse Agilent fluorescence spectrophotometer. Emission quantum yields were determined using L-tryptophan in a degassed aqueous solution as the standard ($\Phi = 0.13$; ex = 280 nm).

Differential scanning calorimetry (DSC) studies were performed on the Netzsch STA 449 F3 Jupiter for experiment A at a rate of 10 °C/min and 1 °C/min, atmosphere: high purity nitrogen. For experiment B, at a heating and cooling rate of 5 °C/min, atmosphere: helium BIP and nitrogen, both experiments in aluminum crucible, with a hole in the lid.

For the RX diffraction studies, crystals of compounds **2**–**7** were obtained by slow evaporation of a dilute MeOH solution. Crystallographic data for compounds were collected on a Bruker SMART APEX DUO three-circle diffractometer equipped with an Apex II CCD detector using MoKα ($\lambda = 0.71073$ Å (Incoatec IμS microsource and Helios optic monochromator); the temperature of collections was − 173 °C (100 K)). Suitable crystals were coated with hydrocarbon oil, picked up with a nylon loop, and mounted the diffractometer. Three standard reflections every 97 reflections were used to monitor the crystal stability. The structure was solved by direct methods; missing atoms were found by difference Fourier synthesis, and refined on F2 by a full-matrix least-squares procedure using anisotropic displacement parameters using SHELX-97. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Copies of available materials can be obtained free of charge on application to the director of CCDC (12 Union Road, Cambridge CB2 IEZ, UK (facsimile: (44) 01223 336033); e-mail: deposit@ccdc.ac.uk).

General procedure for the synthesis of bi-1,2,3-triazoles

The corresponding azide (1 mmol) and alkyne (1 mmol) were added to a solution of glucose (0.045 g, 0.25 mmol) in H_2O (1 mL) and MeOH (5 mL). The mixture was treated successively with the tartrate-NaOH solution (Fehling B solution, 0.1 mL) and $CuSO_4$ solution (Fehling A solution, 0.25 mL, 0.1 mmol). The resulting mixture was stirred at 0 °C for 24 h. The solvent was removed under reduced pressure and the final product was purified by column chromatography (SiO_2, hexane/AcOEt 8:2).

3,3′-Dibenzyl-5, 5′-diphenyl—3H, 3′H-[4,4′] bi [[1,2,3]triazolyl] (**1**). White solid, mp. 110 °C. IR (KBr) ν = 695, 721, 973, 1219, 1296, 1452, 3100 cm^{-1}. ^{1}H RMN: (500 MHz, DMSO-d_6) δ 7.4 (m, 4H), 7.14–7.25 (m, 6H), 7.07–7.20 (m, 6H), 6.81 (d, 4H), 4.81 (d, 2H), 4.74 (d, 2H) ppm. ^{13}C RMN (125 MHz, DMSO-d_6) δ 147.22, 134.04, 129.54, 129.24, 129.07, 128.98, 128.77, 128.36, 125.81, 52.63 ppm; MS [EI$^+$] *m*/*z* (%) 468 [M]$^+$ (40), 349 [M-

Table 1 Synthesis of bi-1,2,3-triazoles

Compound	*R*^{1}	*R*^{2}	% yield
1	CH_2Ph	Ph	68
2	CH_2Ph	$CH_2O(2\text{-}Cl)C_6H_4$	90
3	CH_2Ph	$CH_2O(4\text{-}Cl)C_6H_4$	65
4	CH_2Ph	$CH_2O(4\text{-}Br)C_6H_4$	77
5	CH_2Ph	$CH_2O(4\text{-}CH_3)C_6H_4$	70
6	$(CH_2)_3Ph$	Ph	78
7	CH_2Ph	CH_2OH	50

Table 2 Crystal data and structure refinement of X-ray diffraction for compounds **1**–**7**

Crystal data	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{30}H_{24}N_6$	$C_{32}H_{26}Cl_2N_6O_2$	$C_{32}H_{26}Cl_2N_6O_2$	$C_{32}H_{26}Br_2N_6O_2$	$C_{34}H_{32}N_6O_2$	$C_{34}H_{32}N_6$	$C_{20}H_{20}N_6O_2$
Formula weight	468.55	597.49	597.49	686.41	556.65	524.65	376.42
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	1.54178	1.54178	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	P1	I 2/a
Unit cell dimensions (Å, °)							
a	14.4904(2)	a14.7328(2)	9.5770(3)	9.6573(2)	11.4630(3)	11.1266(2)	14.4382(7)
b	17.7191(3)	10.9886(2)	12.2949(4)	12.5034(3)	8.8404(2)	11.7929(2)	6.8915(3)
c	19.1805(3)	18.2024(3)	13.4636(4)	13.4322(3)	28.9946(8)	12.9785(3)	18.4220(12)
a	81.7410(6)	90	71.3876(6)	70.9453(11)	90	79.4490(6)	90
β	88.3359(7)	105.0665(7)	79.6936(7)	80.2332(11)	95.1982(11)	68.3360(6)	98.4947(8)
γ	82.5681(6)	90	78.2471(6)	77.4414(11)	90	62.7000(6)	90
Volume (Å^3)	4832.43(13)	2845.54(8)	1459.78(8)	1487.80(6)	2926.16(13)	1406.20(5)	1812.89(17)
Z	8	4	2	2	4	2	4
Calculated density, *D* (mgm^{-3})	1.288	1.395	1.359	1.532	1.264	1.239	1.379
F(000)	1968	1240	620	692	1176	556	792
Absorption coefficient, μ (mm^{-1})	0.079	0.270	0.263	2.765	0.081	0.075	0.094
Crystal size (mm^3)	0.37 × 0.36 × 0.19	0.47 × 0.13 × 0.12	0.46 × 0.38 × 0.16	0.25 × 0.23 × 0.09	0.23 × 0.22 × 0.21	0.29 × 0.19 × 0.19	0.284 × 0.256 × 0.118
θ_{max} (°)	27.407	27.103	27.494	27.444	27.445	25.06	25.343
θ_{min} (°)	1.417	2.186	1.770	1.750	2.373	1.69	2.236
h	$-18 \rightarrow 18$	$-18 \rightarrow 18$	$-12 \rightarrow 12$	$-12 \rightarrow 12$	$-14 \rightarrow 14$	$-13 \rightarrow 13$	$-17 \rightarrow 17$
k	$-22 \rightarrow 22$	$-13 \rightarrow 14$	$-15 \rightarrow 15$	$-16 \rightarrow 16$	$-11 \rightarrow 11$	$-14 \rightarrow 14$	$-8 \rightarrow 8$
l	$-24 \rightarrow 24$	$-23 \rightarrow 23$	$-17 \rightarrow 17$	$-17 \rightarrow 17$	$-37 \rightarrow 37$	$-15 \rightarrow 15$	$-22 \rightarrow 22$
Reflections collected	124,519	29,833	27,240	38,281	41,620	21,115	10,014
Independent reflections (R_{int})	21,917 (0.0236)	6276 (0.0305)	6698 (0.0270)	6809 (0.0282)	6657 (0.0209)	4988 (0.0183)	1661 (0.0133)
Data/restraints/parameters	21,917/770/1407	6276/0/379	6698/0/379	6809/0/379	6657/0/381	4988/290/407	1661/1/131
Goodness-of-fit on F^2	1.019	1.034	1.035	1.061	1.036	1.041	1.061
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0401, 0.0965	0.0339, 0.0793	0.0369, 0.0896	0.0348, 0.0864	0.0416, 0.1110	0.0319, 0.0780	0.0326, 0.0812
R_1,[a] wR_2[b] (all data)	0.0455, 0.1004	0.0394, 0.0825	0.0416, 0.0927	0.0409, 0.0895	0.0459, 0.1142	0.0357, 0.0809	0.0342, 0.0825
Residuals, *e*·(Å^{-3})	0.301, −0.229	0.335, −0.255	0.427, −0.559	1.134, −0.894	0.314, −0.264	0.243, −0.187	0.282, −0.178

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$

[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$

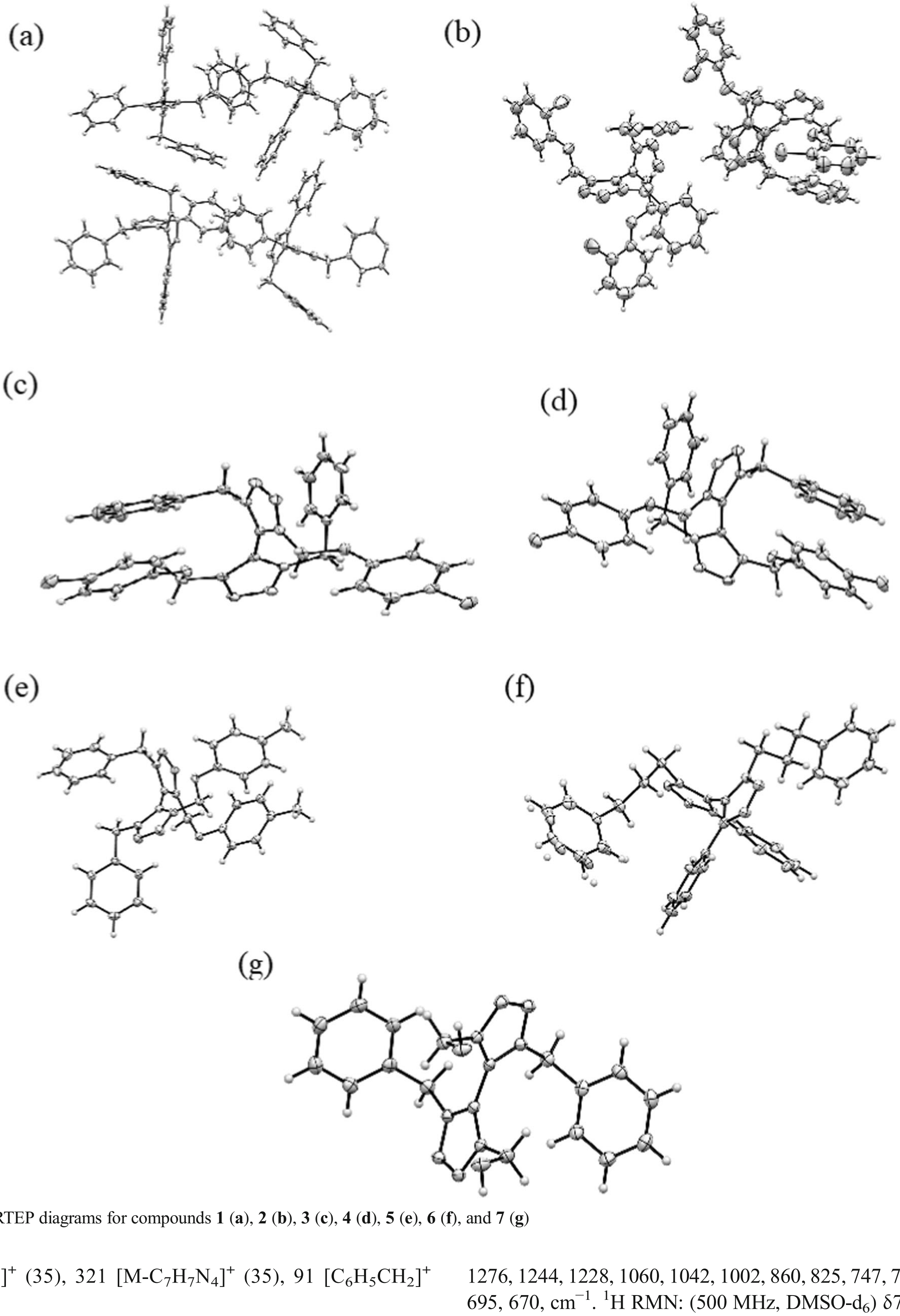


Fig. 1 ORTEP diagrams for compounds **1** (**a**), **2** (**b**), **3** (**c**), **4** (**d**), **5** (**e**), **6** (**f**), and **7** (**g**)

$C_7H_7N_2]^+$ (35), 321 $[M-C_7H_7N_4]^+$ (35), 91 $[C_6H_5CH_2]^+$ (100).

3,3′-Dibenzyl-5,5′-bis-(2-chlorophenoxymethyl)-3H,3′H-[4,4′]bi[[1,2,3]triazolyl] (**2**). White solid mp. 92 °C. IR (KBr) $\nu = 3062$, 3028, 2916, 2850, 1715, 1589, 1484, 1447, 1276, 1244, 1228, 1060, 1042, 1002, 860, 825, 747, 737, 709, 695, 670, cm^{-1}. ^{1}H RMN: (500 MHz, DMSO-d$_6$) δ7.41 (dd, 2H), 7.31 (m, 4H), 7.28 (m, 6H), 7.22 (m 2H), 6.94 (m, 2H), 5.09 (d, 2H) 4.95 (d, 2H), 4.77 (d, 2H) 4.64 (d, 2H) ppm. ^{13}C RMN (125 MHz, DMSO-d$_6$) δ 153.24, 144.65, 134.52,

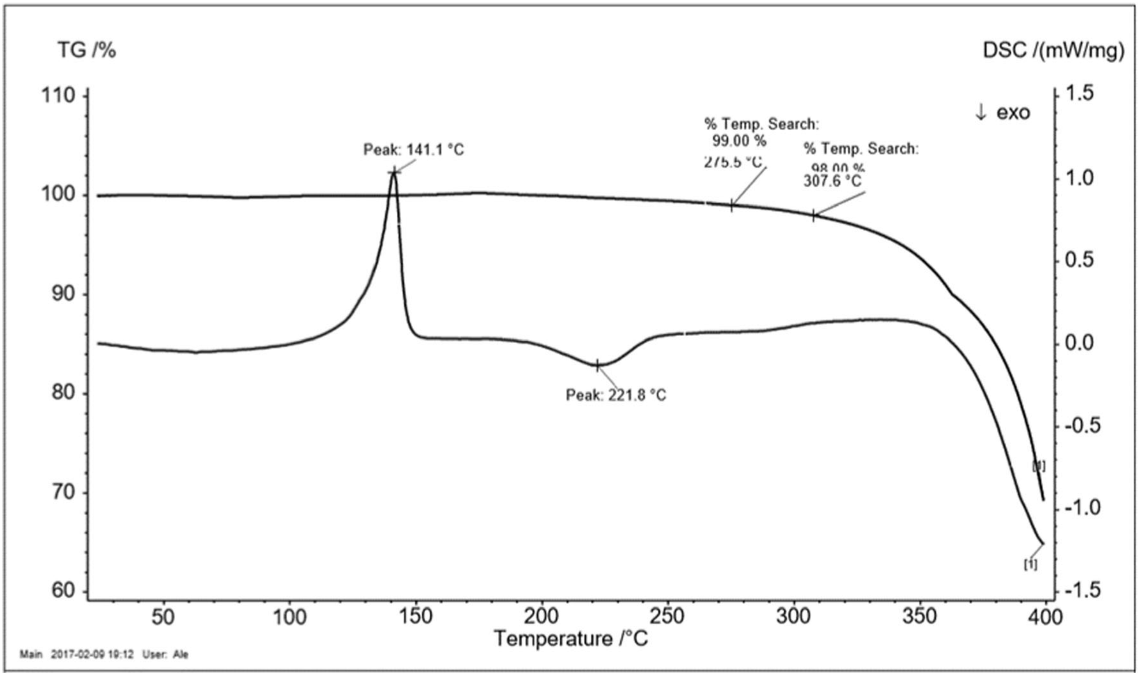


Fig. 2 TG thermogram and DSC curve of compound **1**

130.43, 129.23, 128.58, 128.30, 122.5, 121.65, 114.35, 61.75, 52.44 ppm. MS [EI$^+$] m/z (%) 596 [M]$^+$ (10), 526 [M-Cl$_2$]$^+$ (20), 119 [C$_7$H$_7$N$_2$]$^+$ (20), 91 [C$_7$H$_7$]$^+$ (100). Elemental analysis calculated: C, 64.33; H, 4.39; N, 14.07, found: C, 64.31; H, 4.27; N, 14.05.

3,3′-Dibenzyl-5,5′-bis-(4-chlorophenoxymethyl)-3H,3′H-[4,4′]bi[[1,2,3]triazolyl] (**3**). White solid; mp.70 °C. IR (KBr) ν = 3141, 2925, 2853, 1886, 1731, 1579, 1490, 1239, 1221, 993, 830, 815, 756, 720, 649, 515, 473 cm^{-1}; ^{1}H RMN: (500 MHz, DMSO-d$_6$) δ 7.19-7.34 (m, 14H.) 6.93 (d, 2H)

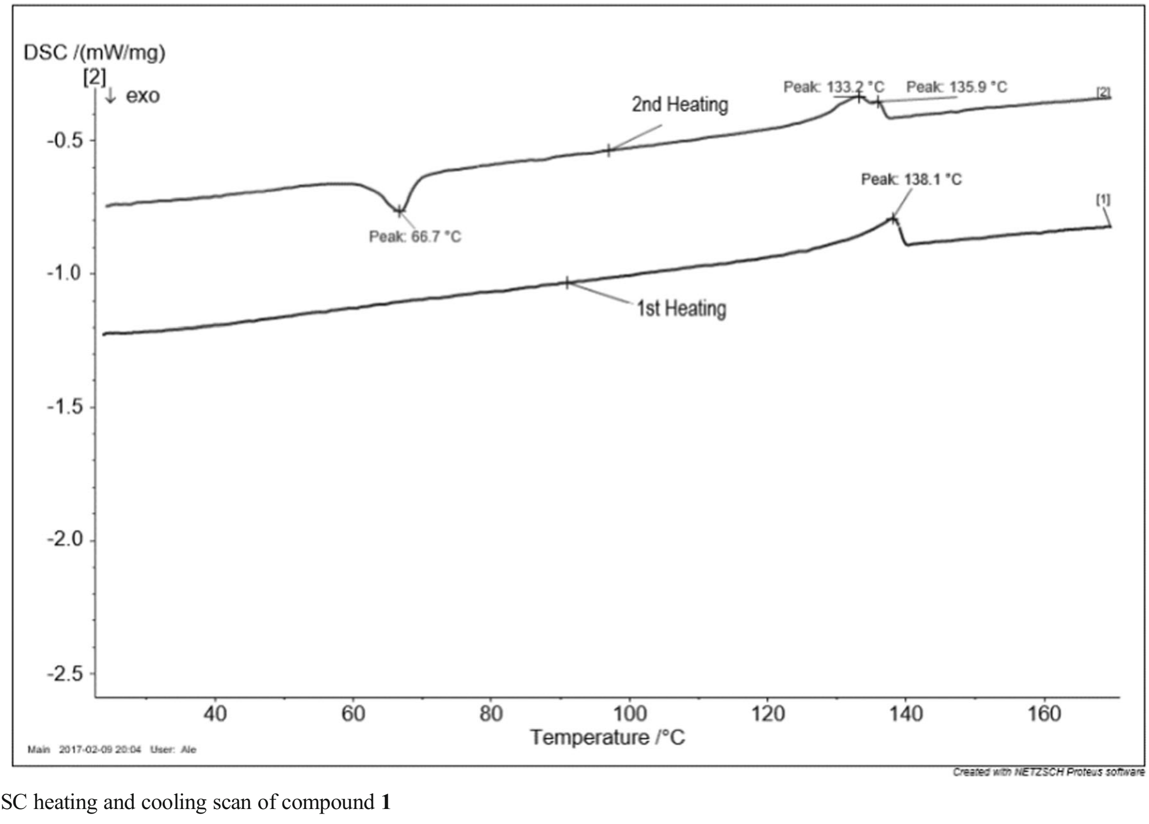


Fig. 3 DSC heating and cooling scan of compound **1**

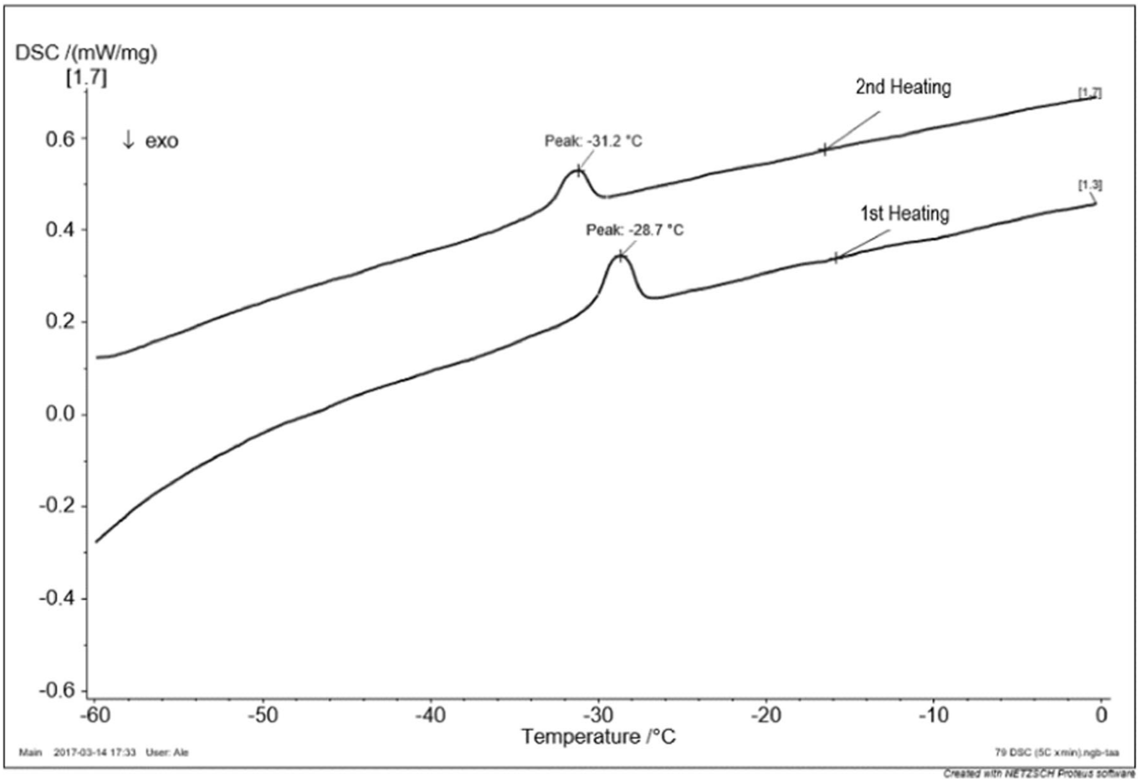


Fig. 4 DSC heating and cooling scan of compound **2**

6.69 (d, 2H) 5.75 (s, 4H) 5.07 (d, 4H) ppm; ^{13}C RMN (125 MHz, DMSO-d$_6$) δ 157.28, 143.15, 136.41, 129.68, 129.22, 128.63, 128.39, 125.21, 117,116.99, 61.81, 53.31 ppm. MS [EI$^+$] *m*/*z* (%) 596 [M]$^+$ (5), 92 [C_7H_8]$^+$ (100). Elemental analysis calculated: C, 64.33; H, 4.39; N, 14.07, found: C, 64.10; H, 4.48; N, 13.77.

3,3′-Dibenzyl-5,5′-bis-(4-bromophenoxymethyl)-3H,3′H-[4,4′]bi[[1,2,3]triazolyl] (**4**). White solid, mp. 68 °C; IR (KBr) $\nu = 2952$, 2922, 2853, 1577, 1483, 1459, 1337,1336, 1285,1237, 1211, 1118, 1000, 858,809, 730, 706, 615, 592, 507 cm^{-1}. ^{1}H RMN: (500 MHz, DMSO-d$_6$) δ 7.39 (m, 4H), 7.17–7.31 (m, 10H), 6.93 (s, 4H), 5.57 (s, 4H) 5.18 (s, 4H) ppm. ^{13}C RMN (125 MHz, DMSO-d$_6$) δ 164.85, 137.3, 133.85, 131.85, 117.7, 114.45, 76.47, 40.21, 39.79, 39.62, 39.45 ppm. MS [EI$^+$] *m*/*z* (%) 684 [M]$^+$ (5), 526 [M-Br$_2$]$^+$ (30), 119 [$C_7H_7N_2$]$^+$ (20), 92 [C_7H_8]$^+$ (100). Elemental analysis calculated: C, 55.99; H, 3.82; N, 12.24, found: C, 55.13; H, 4.00; N, 12.05.

Table 3 Dihedral angles (°) formed by triazole rings in bi-1,2,3-triazoles

Compound	Dihedral angle (°)
1	82.07
2	77.93
3	80.64
4	81.28
5	83.58
6	86.39
7	76.45

3,3′-Dibenzyl-5,5′-bis-p-tolyloxymethyl-3H,3′H-[4,4′]bi[[1,2,3]triazolyl] (**5**) White solid, m.p. 85 °C. IR (KBr) $\nu = 3064$, 3032, 2923, 2857, 1725, 1611, 1568, 1509, 1456, 1290, 1228, 1177, 1027, 1016, 813, 709, 511 cm^{-1}. ^{1}H RMN: (500 MHz, DMSO-d$_6$) δ 7.31 (ddd, 6H), 7.07 (m, 4H), 6.93 (d, 4H), 6.57 (d, 4H), 5.15 (d,

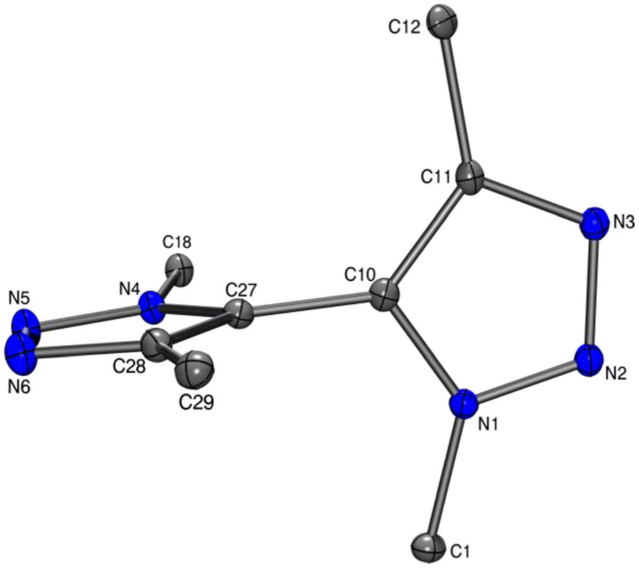


Fig. 5 Orthogonal conformation in the triazole rings in compound **6**

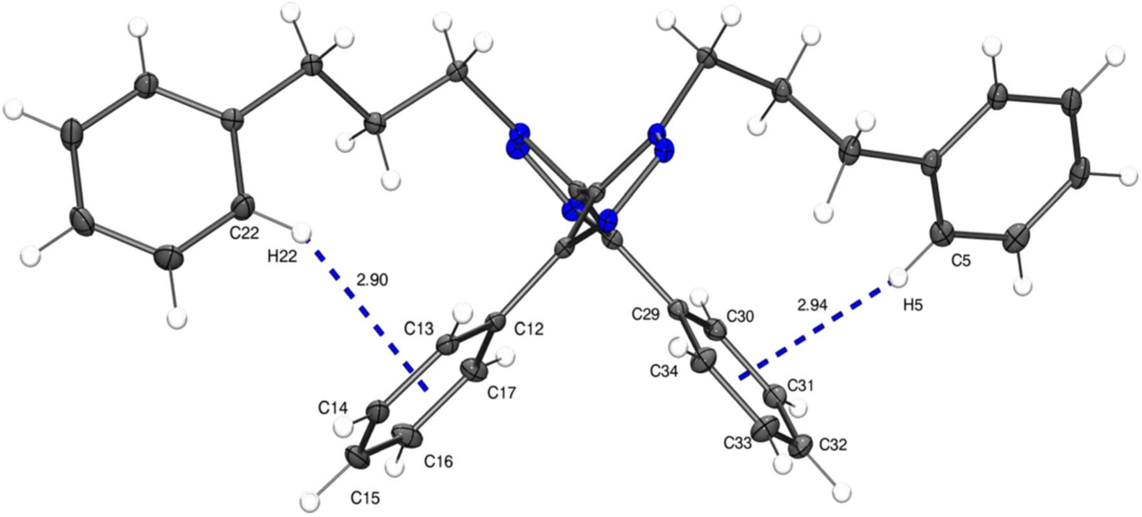


Fig. 6 Intramolecular interactions C–H—pi found in compound **6**

2H), 5.03 (d, 2H), 4.58 (d, 2H), 4.44 (d, 2H), 2.21 (s, 6H) ppm. ^{13}C RMN (125 MHz, DMSO-d$_6$) δ 155.61, 145.39, 134.69, 129.94, 129.28, 128.11, 122.4, 115.40, 114.73, 60.66, 52.25, 20.045 ppm. MS [EI$^+$] *m*/*z* (%) 556 [M]$^+$ (5), 91 [C_7H_7]$^+$ (100). Elemental analysis calculated: C, 72.99; H, 4.98; N, 15.96, found: C, 72.93; H, 4.91; N, 15.95.

5,5′-Diphenyl-3,3′-bis-(3-phenylpropyl)-3H,3′H-[4,4′]bi[[1,2,3]triazolyl] (**6**). White solid, m. p. 131 °C. IR (ATR) $\nu = 2915$, 2862, 1439 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (m, 4H), 7.42–7.20 (m, 2H), 3.79 (dd, 4H), 2.57 (t, 4H), 1.98 (t, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 141.6, 131.9, 129.2, 128.9, 128.6, 127.9, 126.3, 122.8, 49.3, 34.2, 25.7. MS [EI$^+$] *m*/*z* (%) 552 [M]$^+$ (5), 91

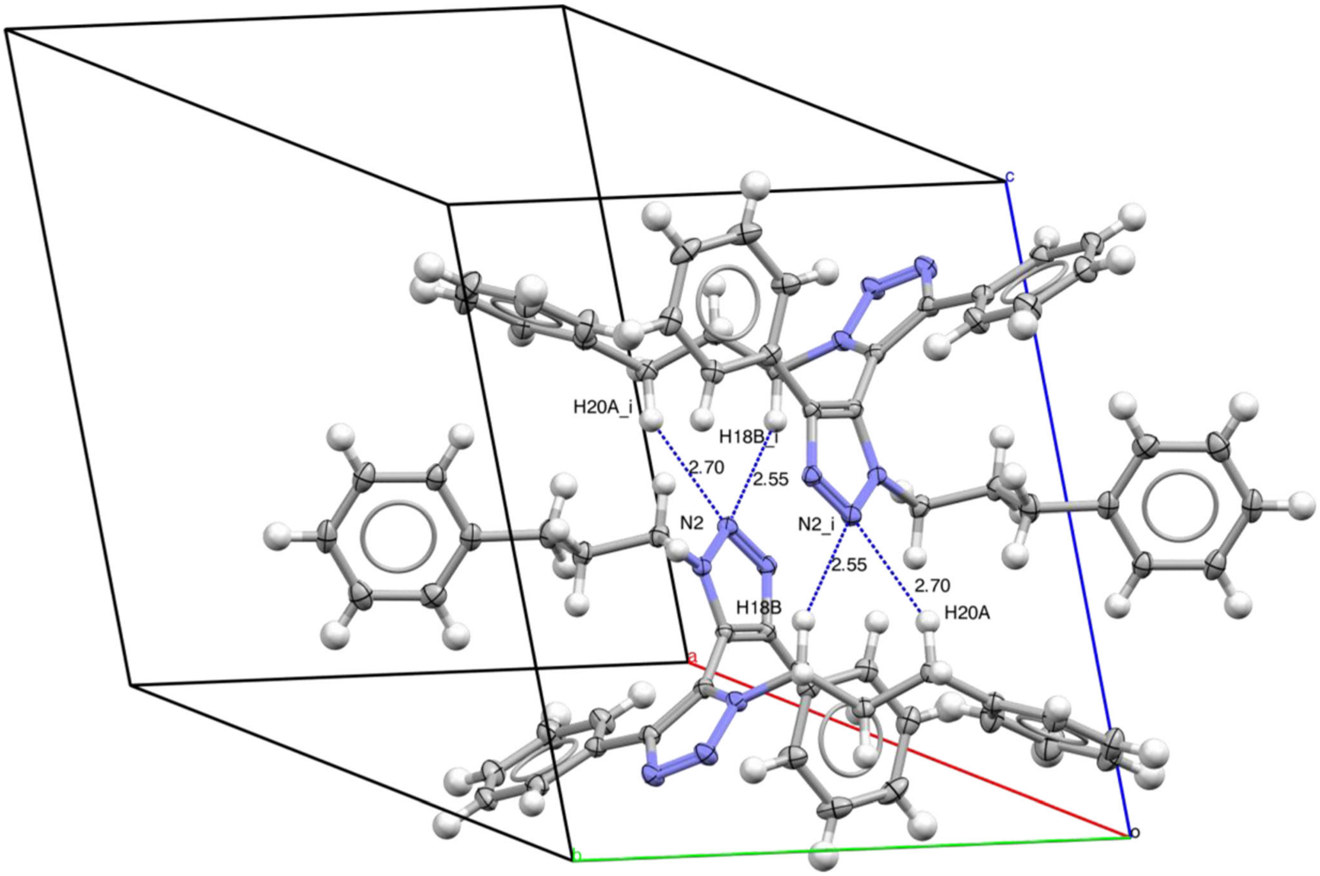


Fig. 7 Dimer formed by the C–H—N2 interaction in the crystal packing of compound **6**. Symmetry code (*i*) = − *x*, 1 − *y*, 1 − *z*

Table 4 Photophysical properties bi-1,2,3-triazoles **1-5** in CH_3OH

Compound	R^2	λ_{max} abs (nm)	Extinction coefficient (M^{-1} cm^{-1})	Emission (nm)[a]	Quantum yield (%)[b]	RFI[c]
1	Ph	244; 286	1.3×10^5; 5.8×10^4	384	10.4	–
2	$CH_2O(2\text{-}Cl)C_6H_4$	243; 262	7.6×10^4; 3.7×10^4;	361	5.8	0.43
3	$CH_2O(4\text{-}Cl)C_6H_4$	242; 263	6.8×10^4; 3.8×10^4	355	5.2	0.40
4	$CH_2O(4\text{-}Br)C_6H_4$	242; 267	5.3×10^4; 3.0×10^4	341	3.4	0.23
5	$CH_2O(4\text{-}CH_3)C_6H_4$	242; 265	3.5×10^4; 1.7×10^4	338	4.5	0.29

[a] $\lambda_{exc} = 286$ nm

[b] Relative to L-tryptophan

[c] *RFI* relative fluorescence intensity normalized with respect to **1**

$[C_7H_7]^+$ (100). Elemental analysis calculated: C, 78.23; H, 6.57; N, 15.21, found: C, 78.29; H, 6.52; N, 15.16.

(3,3′-Dibenzyl-5′-hydroxymethyl-3H,3′H-[4,4′]bi[[1,2,3]triazolyl]-5-yl)-methanol (**7**) White solid, m.p. 85 °C. IR (KBr) $v = 3350$, 2923, 2857, 1611, 1568, 1509, 1456, 1290, 1230 cm^{-1}. ^1H RMN: (500 MHz, DMSO-d_6) δ 7.31 (ddd, 6H), 7.07 (m, 4H), 6.93 (d, 4H), 6.57 (d, 4H), 5.15 (d, 2H), 5.03 (d, 2H), 4.58 (d, 2H), 4.44 (d, 2H) ppm. ^{13}C RMN (125 MHz, DMSO-d_6) δ 141.4, 136.8, 129.94, 129.3, 128.1, 121.9, 59.7, 52.1 ppm. MS $[EI^+]$ *m/z* (%) 376 $[M]^+$ (5), 375 $[M\text{-}H]^+$ (10), 92 $[C_7H_8]^+$ (100). Elemental analysis calculated: C, 63.82; H, 5.36; N, 22.33, found: C, 63.83; H, 5.29; N, 22.25.

Results and discussion

The initial experiments were aimed to prepare bi-1,2,3-triazoles through an adaptation of a previous work by our group (Scheme 1) [11, 38]. Thus, treatment of diverse azides with the appropriate alkynes in the presence of catalytic amounts of a Fehling Reagent-glucose-NaOH system at 0 °C afforded the corresponding bi-1,2,3-triazoles **1**–**7** in 65–90% yields (Table 1).

Compounds **1**–**7** were fully characterized by the conventional spectroscopic techniques. Moreover, these compounds were crystalline solids suitable for X-ray crystallography studies. Crystallographic data and structural refinement parameters of compounds **1**–**7** are summarized in Table 2 and the corresponding ORTEP representations are shown in Fig. 1, confirming the proposed structure for these compounds.

Single-crystal X-ray diffraction analysis performed on compounds **1**–**7** revealed some interesting facts. For example, crystal structure of bi-1,2,3-triazole **1** represents a new polymorphic form of this compound which previously crystallized in an orthorhombic crystal system under a centrosymmetric space group Pbca [11]. In this case, the new polymorph of **1** crystallized in a triclinic crystal system under a space group P-1$\bar{1}$ with 4 molecules in the asymmetric unit, two of them displaying disorder in the phenyl moiety (molecule a in Fig. 1). In order to corroborate the presence of polymorphs in compound **1**, simultaneous TGA and DSC studies were determined with a heating rate of 10 °C/min (Fig. 2). TG thermogram of **1** shows only an important weight loss which takes place at above 350 °C associated to the molecule degradation and demonstrating that this product is neither a solvated, nor a hydrated form of compound **1**, while the DSC curve of this sample displays an endothermic process at 141.1 °C. A second sample was analyzed under a cycle plotted in

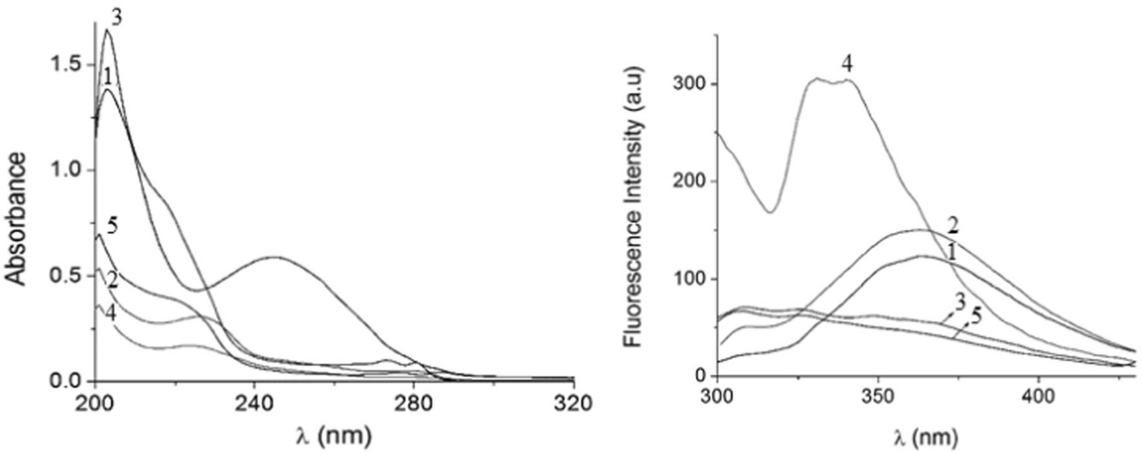


Fig. 8 Absorption and fluorescence spectra of compounds **1**–**5** (10 μM and 2 μM for UV-vis and fluorescence respectively, $\lambda_{ex} = 280$ nm) in CH_3OH

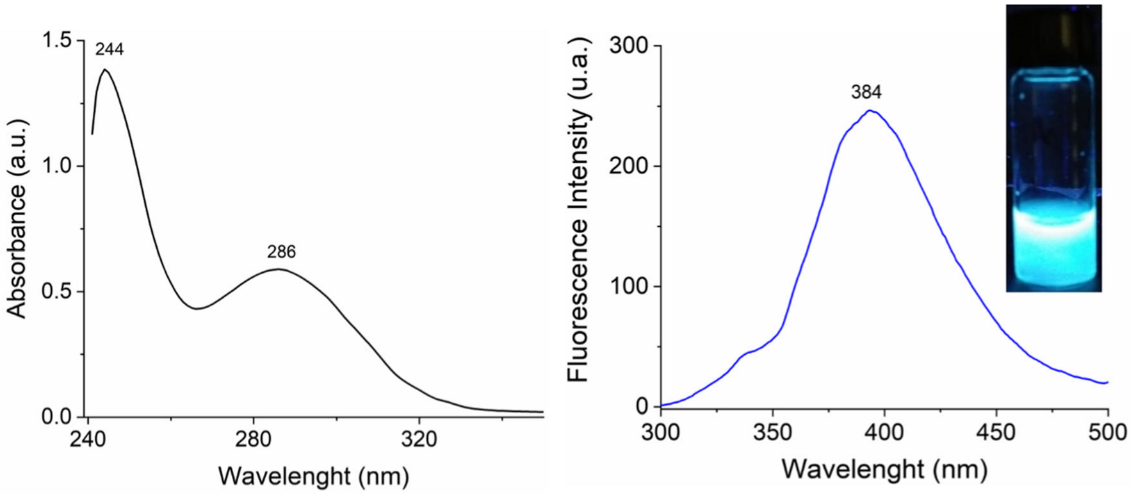


Fig. 9 Absorption (**a**) and fluorescence (**b**) spectra of **1** (10 μM and 2 μM for UV-vis and fluorescence respectively, $\lambda_{ex} = 280$ nm) in CH_3OH. The inset shows solution of A under irradiation at 365 nm UV light

Fig. 3 (heating-cooling-heating rates of 1 °C/min); the DSC scan shows three small endothermic peaks of crystallization at 133.2, 135.9, and 138.1 °C which indicate the existence of 3 polymorphic forms.

A similar behavior was observed in compound **2**, which crystallized with 2 molecules in the asymmetric unit (molecule b in Fig. 1). Two polymorphs were detected in compound **2** through a DSC heating-cooling cycle curve analysis which exhibits two small endothermic peaks of crystallization at − 28.7 °C and − 31.2 °C respectively (Fig. 4).

A noteworthy feature found in compounds **1**–**7** is an almost orthogonal conformation between triazole rings similar to other reported bi-1,2,3-triazoles [5]. Dihedral angles formed by triazole rings are presented in Table 3 and exhibit a range from 76.45 to 86.39°.

For example, dihedral angle N(1)-C(10)-C(27)-N(4) in compound **6** is 86.39(13)° (Fig. 5). In addition, the presence of a C–H—pi interaction between the C(22)-H(22) and the centroid of phenyl ring at 5-position of triazole determines a distance of 3.7658(17) Å between these two elements and a dihedral angle C(10)-C(11)-C(12)-C(17) of 23.84(17)° (Fig. 6). Similar distance and dihedral angle are observed from interactions of the opposite C(5)-H(5)/5′-phenyl-1′,2′,3′-triazolyl system. These elements suggest the presence of a rigid axially structure along C10–C27 bond which is favored by the C–H—pi interactions.

In the crystal packing some intermolecular interactions have been found. C-H—N2 interactions, C(20)i-H(20A)i—N(2) and C(18)i-H(18B)i—N(2) H—N are 2.55 and 2.70 Å respectively forming a dimer in the unit cell as a show in the Fig. 7. The angles C–H–N are close to 150°, the distance ppC(20)i-N(2) is 3.5913(14) Å, and the distance C(18)i-N(2) is 3.4728(13) Å with a symmetry code (*i*) $-x$, $1-y$, $1-z$.

1,2,3-Triazole-based molecular compounds have shown a large diversity of photophysical properties as a function of small structural changes; an example is the regioisomerism which dramatically modifies the molecular absorption and emission attributes in these compounds [25, 32]. Taking this point into consideration, we explored the effect of substituent $-R^2$ (see Table 1) on the photophysical properties of bi-1,2,3-triazoles **1**–**5**. The basic photophysical properties (absorption maxima, emission, and quantum yields) of **1**–**5** in methanolic solutions are collected in Table 4 and the corresponding UV-vis and fluorescence spectra are plotted in Fig. 8.

All compounds display good solubility in methanol and the corresponding solutions were used for further studies. Compound **1** exhibits a strong blue emission under ambient conditions with bands centered at 384 upon excitation at 286 nm, as shown in Fig. 9. Solutions of **2**–**3** present a modest emission at 361 and 355 nm respectively. In contrast, compounds **4**–**5** display very low fluorescence. One particular point is that insertion of an electron-donating group (halophenoxymethyl groups in compounds **2**–**4** and tolyloxymethyl group in compound **5** at the C-4 triazole position in 1,1′-dibenzyl-bis(1,2,3-triazole) fragment induces a considerable quenching of the emission accompanied by significant blue-shift of 23-46 nm in the position of the longest wavelength bands.

According to RFI parameter with respect to bi-1,2,3-triazole **1**, the effect of substitution of the bi-1,2,3-triazole core on the decrease in the emission can be described as phenyl > 2-chlorophenoxymethyl > 4-chlorophenoxymethyl > tolyloxymethyl. This trend is consistent with the quantum yield values determined (Table 4). Similar photochemical properties with UV/blue-light emission in the range of 316–422 nm have been reported previously for a series of aryl-1,2,3-triazoles derivatives with Stokes shift in the range of 38–94 nm [39]. Thus, the emission performance effect of substituent group at C-4 position on 3,3′- dibenzyl -5, 5′-diphenyl-bi-1,2,3-triazolyl fragment as a fluorescence core can be elucidated as follows: (1) the emission is considerably higher when bi-1,2,3-triazole fragment contains rigid substituents such as phenyl. It is well known that rigidity increase in small fluorescent molecules reduces the energy loss through non-radiative processes such as vibrations [39, 40]; (2) a significant quenching is observed by insertion of electro-donating groups; this optical effect is not unexpected, because the emission in organic fluorophores is favored by the combination of a strongly electron-donating moiety conjugated through to π-linker to a strongly electron-accepting one (push-pull system) [41, 42]; and (3) the highest fluorescent emission in bi-1,2,3-triazole **1** compared with the other studied compounds can be assigned to a good conjugation between phenyl group and triazole ring (dihedral angles between 0.5 and 20°). These results reveal the potential influence of some C-4 substituent groups on photophysical properties of bi-1,2,3-triazole derivatives. Hence, the strong emission of **1** is possible through a combination provided by a straightforward synthesis from the click chemistry approach, turning this molecule into a promising candidate for the design of more sophisticated blue-light-emitting molecules.

Conclusion

In summary, the structure of some bi-1,2,3-triazoles was elucidated, showing dihedral angles in the crystalline structure of some bi-1,2,3-triazoles which suggest the presence of a rigid axially chiral structure, and therefore, atropisomers, such as Zhu and coworkers have proposed for other bi-1,2,3-triazoles [5]. This rigidity, in combination with a significant conjugation effect through homocyclic and heterocyclic rings, also produces an outstanding fluorescent emission in bi-1,2,3-triazole **1** that has not been registered in this kind of compounds and will open new study lines about these molecules. The elements herein described suggest that bi-1,2,3-triazoles will enjoy widespread applications in the future.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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