Synthesis and Spectral Properties of Novel Fluorescent Diethoxycarbonyl Glycoluril Derivatives

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Abstract: A novel class of fluorescent diethoxycarbonyl glycoluril derivatives with aryl alkyne side chains was synthesized via alkylation and subsequent Sonogashira cross-coupling reactions. The fluorescence spectra showed that these compounds exhibited good blue fluorescence with the maximum wavelengths ranging from 368 nm to 403 nm.

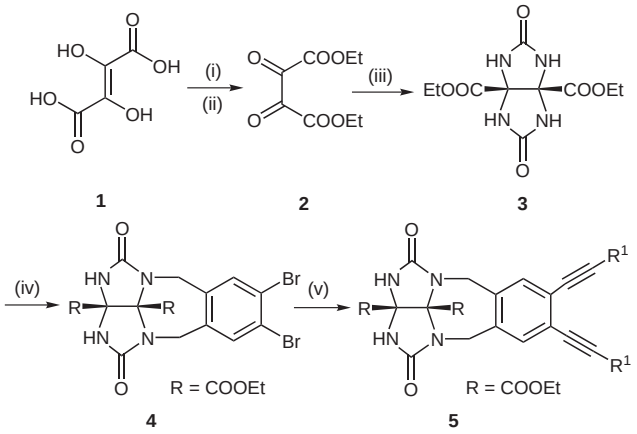
Key words: diethoxycarbonyl glycoluril, aryl alkyne, Sonogashira cross-coupling, fluorescence

The development of fluorescent sensors capable of selectively detecting chemical species including cations[1] and anions[2] has always been of particular interest due to high sensitivity and selectivity,[3] 'on–off' switchability and hence their use as logic gates,[4] and convenient monitoring of molecular-level events through light signals. A fluorescent sensor typically consists of three components, which are a recognition part that binds the target analyte, a readout part that signals binding, and a linker that connects the recognition part and the readout part. In the case of anion sensors, hydrogen-bonding groups have been widely used in binding sites for anion recognition. Hydrogen-bonding sites typically used in fluorogenic chemosensors are ureas,[5] thioureas,[6] calyx[4]pyrroles,[7] sapphyrins,[8] porphyrins,[9] and amides.[10]

Glycolurils, due to their special precaved structure, were widely used as platforms or building blocks to construct a series of compounds with more sophisticated structures in the past decades.[11] On the other hand, glycoluril derivatives have been used in a variety of applications including polymer cross-linking, psychotropic agents, explosives, in the stabilization of organic compounds against photodegradation, textile waste stream purification, and combinatorial chemistry.[12] However, one area of glycoluril derivatives that has been less well explored is their utilization as fluorescent chemosensors for anions.[13]

One of our research interests is to develop a new generation of potential fluorescent anion sensors based on the diethoxycarbonyl glycoluril. We used Sonogashira coupling[14] to attach terminal aryl alkynes covalently to aromatic sidewalls of glycoluril derivative **4** and build π-systems that can be used as the signaling subunit and used two ureidyl N–H that can act as the binding sites. We believe that complexation will take place between these fluorescent derivatives containing two ureidyl N–H groups and the corresponding anion through hydrogen-bonding interactions.

The synthetic route used to obtain fluorescent derivatives **5a**–**h** is shown in Scheme 1. Most glycolurils have poor solubility in common organic solvents. In order to solve the solubility problem, the more organic soluble diethoxycarbonyl glycoluril **3** was synthesized according to the literature procedure[15] and used for these studies. Compound **3** was alkylated with 1,2-bis(bromomethyl)-4,5-dibromobenzene using *t*-BuOK as base in anhydrous DMSO to give **4** in 59% yield. The coupling reaction between **4** and a number of terminal alkynes was readily accomplished using $Pd(PPh_3Cl_2)_2$ and CuI as catalysts in the presence of Et_3N in DMF at 100 °C, and the expected compounds **5a**–**h**, a novel class of fluorescent diethoxycarbonyl glycoluril derivatives, were obtained.



Scheme 1 *Reagents and conditions*: (i) AcOH, Br_2, H_2O; (ii) EtOH, HCl (g), 0 °C; (iii) PhH, H_2NCONH_2, TFA, reflux; (iv) 1,2-bis(bromomethyl)-4,5-dibromobenzene, *t*-BuOK, DMSO; (v) $R^1C{\equiv}CH$, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, DMF.

A variety of substrates were used in this reaction (Table 1). Taking into consideration that the nature of the substituents in phenylacetylene could affect the fluorescence intensity and emission wavelength, we have synthesized five different *para*-substituted phenylacetylenes,[16] 4-ethynylpyridine[17] and 3-ethynylpyridine.[17] The experimental results showed that the yields were not affected drastically in the presence of either electron-donating or

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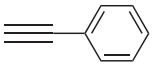
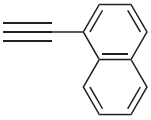
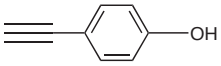
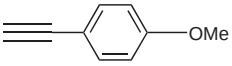
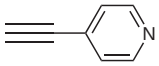
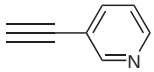
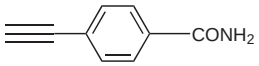
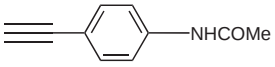
electron-withdrawing groups on phenylacetylene. All reaction products gave satisfactory ^{1}H NMR, ^{13}C NMR, MS and IR data.[18] In addition, the structure and conformation of compound **5a**, was further elucidated by single-crystal X-ray diffraction,[19] as shown in Figure 1. The compound has a well-defined geometry due to the rigidity that the fused rings confer on the molecule. The angle between the mean planes defined by the five-membered rings is 116.9°. The distance between two carbonyl oxygen atoms (O_1–O_2) of the glycoluril moiety is 5.70 Å. Interestingly, one of the ethynyl is tortuose with a torsion angle of 170.1°. The phenyl ring C (C1–C6) of the sidewall and phenyl ring D (C9–C14) of the side chain are essentially coplanar with a dihedral angle of 3.7°. The phenyl ring C (C1–C6) is twisted with respect to ring E (C17–C22) making a dihedral angle of 13.5°.

Table 1 Synthesis of Fluorescent Derivatives **5a**–**h** from Terminal Aryl Alkynes

Entry	R^1	Product	Yield (%)[a]
1		**5a**	75
2		**5b**	70
3		**5c**	78
4		**5d**	80
5		**5e**	69
6		**5f**	65
7		**5g**	73
8		**5h**	70

[a] Isolated yield.

The photophysical properties of compounds **5a**–**h** were examined in dilute acetonitrile solution (10^{-5} M) and are summarized in Table 2. The emission spectra of **5a**–**h** in acetonitrile solution (1×10^{-5} M) are presented in Figure 2. It was found that **5a**, **5e** and **5f** exhibited a similar λ_{max} of emission (368–370 nm). Fluorescence maximum wavelengths of other derivatives differed from each other. Compared to **5a** with an emission maximum at 370 nm, the emission spectrum of **5b** exhibited a 32 nm bathochromic shift due to the larger π-conjugation of the naphthyl group as compared to that of the phenyl groups of **5a**.

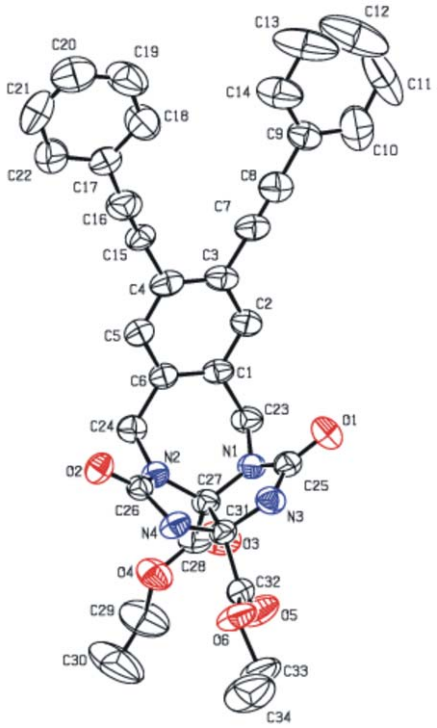


Figure 1 X-ray crystal structure of compound **5a**; hydrogen atoms and solvent molecules are omitted for clarity

Table 2 Absorption and Fluorescence Data of **5a–h**

Compound	λ^{abs}_{max} (nm)[a]	λ^{em}_{max} (nm)[a]	Relative fluorescence
5a	278	370	2.4
5b	316	402	4.6
5c	292	394	4.2
5d	292	392	4.7
5e	275	368	1.4
5f	275	370	1.0
5g	290	385	2.6
5h	300	403	6.6

[a] Measured in acetonitrile.

Similarly, red shifts of **5c**, **5d** and **5h** with respect to **5a** were presumably attributed to the more electron-donating nature of the substituent groups.

In summary, we have synthesized a novel class of fluorescent diethoxycarbonyl glycoluril derivatives with aryl alkyne side chains via alkylation and subsequent Sonogashira cross-coupling reactions. Moreover, their absorption and fluorescence in acetonitrile solution were studied. They exhibited different emitting fluorescence wavelengths ranging from 368 nm to 403 nm. Further studies on the chemosensor behavior of the new generation of fluorescent derivatives toward various anions are underway in our laboratory.

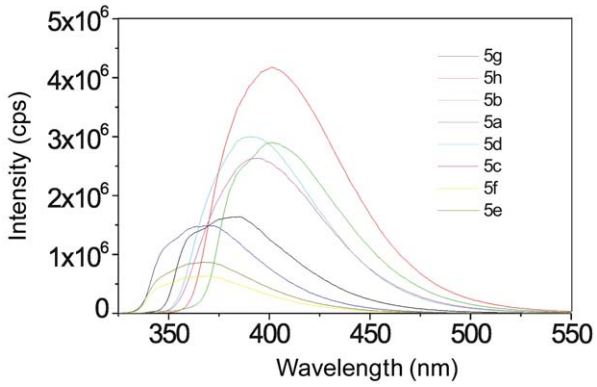


Figure 2 The fluorescence emission spectra of **5a**–**h** in acetonitrile solution (1×10^{-5} M)

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(18) **General Procedure for the Synthesis of Compounds 5**: To a solution of $Pd(PPh_3)_2Cl_2$ (36 mg, 0.05 mmol), CuI (19 mg, 0.10 mmol) and compound **4** (273 mg, 0.50 mmol) in freshly distilled Et_3N (15 mL) and DMF (25 mL) under Ar atmosphere at r.t., were added phenylethynylene (204 mg, 2 mmol). The mixture was warmed to 100 °C for 14 h (monitored by TLC), and then the solvent was removed under reduced pressure. The solid residue was purified by flash chromatography (SiO_2, CH_2Cl_2–MeOH, 50:1) to give **5a** (221 mg, 0.375 mmol, 75%) as a white solid. Compound **5a**: IR (KBr): 3405 (w), 3213 (w), 3066 (w), 2981 (w), 1758 (s), 1724 (s), 1709 (s), 1468 (m), 1282 (s), 1091 (m), 1032 (m), 758 (s), 689 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.56 (m, 12 H), 5.99 (s, 2 H), 4.85 (d, *J* = 16.0 Hz, 2 H), 4.43 (d, *J* = 16.0 Hz, 2 H), 4.33 (q, *J* = 6.8 Hz, 2 H), 4.26 (q, *J* = 6.8 Hz, 2 H), 1.34 (t, *J* = 6.8 Hz, 3 H), 1.31 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.77, 165.46, 156.89, 135.97, 132.75, 131.70, 128.55, 128.36, 125.66, 123.00, 94.95, 87.53, 82.88, 73.47, 63.72, 63.40, 44.29, 13.98, 13.82. ESI–MS: *m*/*z* = 588.9 $[M + H]^+$, 611.0 $[M + Na]^+$. Compound **5b**: IR (KBr): 3418 (w), 3059 (w), 2981 (w), 2822 (w), 1759 (s), 1733 (s), 1702 (s), 1466 (s), 1426 (m), 1274 (m), 1136 (w), 804 (w), 774 (s) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 8.61 (s, 2 H), 8.40 (d, *J* = 8.4 Hz, 2 H), 8.05 (d, *J* = 8.4 Hz, 2 H), 7.99 (d, *J* = 8.4 Hz, 2 H), 7.88 (d, *J* = 7.2 Hz, 2 H), 7.81 (s, 2 H), 7.57 (q, *J* = 8.0 Hz, 2 H), 7.50 (d, *J* = 7.2 Hz, 2 H), 7.12 (q, *J* = 8.0 Hz, 2 H), 4.79 (d, *J* = 16.0 Hz, 2 H), 4.58 (d, *J* = 16.0 Hz, 2 H), 4.28 (q, *J* = 7.2 Hz, 2 H), 4.17 (q, *J* = 7.2 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.45, 166.00, 157.10, 138.50, 132.89, 132.82, 132.43, 131.01, 129.66, 128.53, 127.19, 126.77, 125.65, 125.52, 123.73, 119.39, 92.46, 91.85, 82.37, 74.19, 62.96, 62.72, 43.37, 13.84, 13.78. ESI–MS: *m*/*z* = 689.1 $[M + H]^+$, 711.1 $[M + Na]^+$. Compound **5c**: IR (KBr): 3363 (s), 3261 (s), 3039 (w), 2984 (w), 2209 (w), 1769 (s), 1710 (s), 1691 (s), 1605 (s), 1514 (s), 1481 (s), 1267 (s), 1226 (m), 1144 (w), 1038 (w), 838 (w), 754 (w) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 10.01 (s, 2 H), 8.55 (s, 2 H), 7.49 (s, 2 H), 7.39 (d, *J* = 8.4 Hz, 4 H), 6.82 (d, *J* = 8.4 Hz, 4 H), 4.65 (d, *J* = 16.0 Hz, 2 H), 4.48 (d, *J* = 16.0 Hz, 2 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 4.15 (q, *J* = 7.2 Hz, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.41, 157.03, 137.44, 133.09, 132.09, 123.89, 120.56, 115.93,

112.25, 94.54, 85.89, 82.28, 74.10, 62.88, 43.30, 13.75. ESI–MS: *m*/*z* = 621.2 $[M + H]^+$, 643.2 $[M + Na]^+$. Compound **5d**: IR (KBr): 3347 (w), 3219 (w), 2981 (w), 2937 (w), 2207 (w), 1760 (s), 1742 (s), 1710 (s), 1604 (m), 1513 (s), 1467 (m), 1289 (m), 1247 (s), 1140 (m), 1028 (s), 832 (m), 753 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (s, 2 H), 7.41 (d, *J* = 8.8 Hz, 4 H), 6.81 (d, *J* = 8.8 Hz, 4 H), 6.14 (s, 2 H), 4.75 (d, *J* = 16.0 Hz, 2 H), 4.33 (d, *J* = 16.0 Hz, 2 H), 4.24 (q, *J* = 7.2 Hz, 2 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 3.76 (s, 6 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.22 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.84, 159.82, 156.96, 135.58, 133.16, 132.54, 125.73, 115.24, 114.04, 94.46, 86.55, 76.25, 63.71, 55.31, 44.32, 13.99. ESI–MS: *m*/*z* = 649.2 $[M + H]^+$, 671.3 $[M + Na]^+$. Compound **5e**: IR (KBr): 3375 (w), 3061 (w), 2849 (w), 1754 (s), 1731 (s), 1702 (s), 1595 (s), 1458 (s), 1284 (m), 1136 (w), 1032 (w), 821 (w), 767 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.62 (d, *J* = 4.8 Hz, 4 H), 7.61 (s, 2 H), 7.37 (d, *J* = 4.8 Hz, 4 H), 6.08 (s, 2 H), 4.87 (d, *J* = 16.0 Hz, 2 H), 4.46 (d, *J* = 16.0 Hz, 2 H), 4.34 (q, *J* = 7.2 Hz, 2 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 1.35 (t, *J* = 7.2 Hz, 3 H), 1.29 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.35, 156.68, 149.89, 137.24, 133.25, 130.88, 125.42, 124.90, 91.71, 91.34, 82.78, 82.45, 63.65, 44.24, 14.01. ESI–MS: *m*/*z* = 591.1 $[M + H]^+$, 613.0 $[M + Na]^+$. Compound **5f**: IR (KBr): 3576 (w), 3203 (w), 2975 (w), 2938 (w), 2677 (m), 1759 (s), 1703 (s), 1474 (m), 1278 (m), 1033 (m), 807 (w), 768 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 2 H), 8.59 (s, 2 H), 7.81 (d, *J* = 8.0 Hz, 2 H), 7.58 (s, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 6.97 (s, 2 H), 4.85 (d, *J* = 16.0 Hz, 2 H), 4.43 (d, *J* = 16.0 Hz, 2 H), 4.32 (q, *J* = 7.2 Hz, 2 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 1.33 (t, *J* = 7.2 Hz, 3 H), 1.26 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.82, 165.50, 157.05, 152.00, 148.83, 138.49, 136.84, 132.96, 124.94, 90.98, 90.47, 82.74, 73.67, 63.64, 63.42, 44.18, 13.99, 13.81. ESI–MS: *m*/*z* = 591.1 $[M + H]^+$, 613.0 $[M + Na]^+$. Compound **5g**: IR (KBr): 3355 (s), 3200 (s), 2984 (w), 1753 (s), 1703 (s), 1711 (s), 1665 (s), 1609 (s), 1466 (m), 1408 (m), 1391 (m), 1279 (m), 1031 (w), 856 (w), 773 (w) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 8.60 (s, 2 H), 8.09 (s, 2 H), 7.94 (d, *J* = 8.0 Hz, 4 H), 7.67 (d, *J* = 8.0 Hz, 4 H), 7.65 (s, 2 H), 7.51 (s, 2 H), 4.71 (d, *J* = 16.0 Hz, 2 H), 4.53 (d, *J* = 16.0 Hz, 2 H), 4.26 (q, *J* = 7.2 Hz, 2 H), 4.15 (q, *J* = 7.2 Hz, 2 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ =167.02, 166.39, 165.94, 157.01, 138.62, 134.49, 132.62, 131.24, 128.01, 124.61, 123.48, 93.43, 89.14, 82.24, 74.12, 62.90, 62.67, 43.28, 13.75. ESI–MS: *m*/*z* = 675.2 $[M + H]^+$, 697.2 $[M + Na]^+$. Compound **5h**: IR (KBr): 3321 (m), 3103 (w), 3042 (w), 2983 (w), 2210 (w), 1707 (s), 1594 (m), 1525 (s), 1465 (m), 1404 (w), 1371 (w), 1313 (s), 1257 (m), 1033 (w), 836 (w), 764 (w) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 10.18 (s, 2 H), 8.56 (s, 2 H), 7.66 (d, *J* = 8.4 Hz, 4 H), 7.53 (d, *J* = 8.4 Hz, 4 H), 7.50 (s, 2 H), 4.68 (d, *J* = 16.0 Hz, 2 H), 4.49 (d, *J* = 16.0 Hz, 2 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 4.15 (q, *J* = 7.2 Hz, 2 H), 2.07 (s, 6 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.62, 165.91, 156.97, 140.05, 137.77, 132.21, 132.06, 123.76, 118.92, 116.07, 94.15, 86.79, 82.27, 74.07, 62.84, 62.61, 43.28, 24.06, 13.75. ESI–MS: *m*/*z* = 703.2 $[M + H]^+$, 725.2 $[M + Na]^+$.

(19) **Crystal Data for Compound 5a**: $C_{35}H_{32}N_4O_7$, MW = 620.65, triclinic, *a* = 10.133(12), *b* = 11.903(13), *c* = 14.938(17) Å, *α* = 68.396(2)°, *β* = 77.801(2)°, *γ* = 67.511(2)°, *V* = 1543(3) $Å^3$, *T* = 292(2) K, space group $P\bar{1}$, *Z* = 2, μ(Mo–Kα) = 0.094 mm^{-1}, 5369 reflections measured, 2915 unique (R_{int} = 0.1322) which were used in all calculations. The final wR_2 (F_2) was 0.1957 (all data). CCDC-650493 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 (1223)336033; email: deposit@ccdc.cam.ac.uk.