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BINOL-Linked 1,2,3-Triazoles: An Unexpected Fluorescent Sensor with Anion-π Interaction for Iodide Ion

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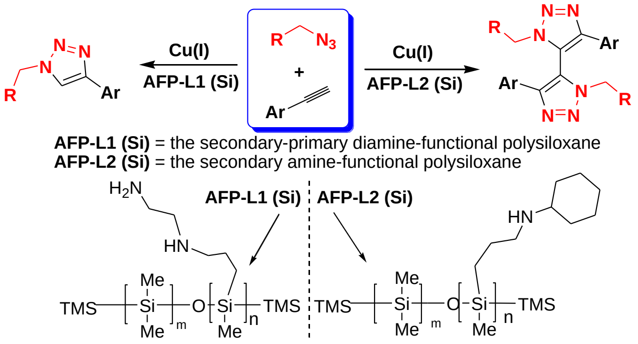
A new family of cyclic and acyclic BINOL-derived triazoles has been prepared for the organocatalytic silylation and subsequent use of fluorescent sensor, in which this type of receptors can recognize I^- with good selectivity unexpectedly. The spectra analysis, including UV and NMR titration, demonstrated that anion-π interaction of I^- to the triazole ring was responsible for the formation of weakly charge-transfer-complex.

The copper(I)-catalyzed Huisgen [3+2] cycloaddition[1] of terminal alkyne and azide reactants, has been broadly known as the "click"-reaction or CuAAC-reaction since 2001/2002.[2-3] Especially for recently, it has become one of the most important methods for heterocyclic ring formation because of its high atom-economic transformation and mild conditions, have found a widespread application in chemistry and advanced material.[4] For example, many molecules with triazoles motif have been become increasingly important building blocks and linkers in drug and medicinal chemistry, and catalysis.[5] More interestingly, a broad variety of triazole-based compounds have been introduced as ligand in transition metal catalysis as there are thermally stable and achieved easily.[6] Besides, the direct use of triazoles as an organocatalyst was also disclosed in several transformations that promoted by the progress of organocatalysis.[7]

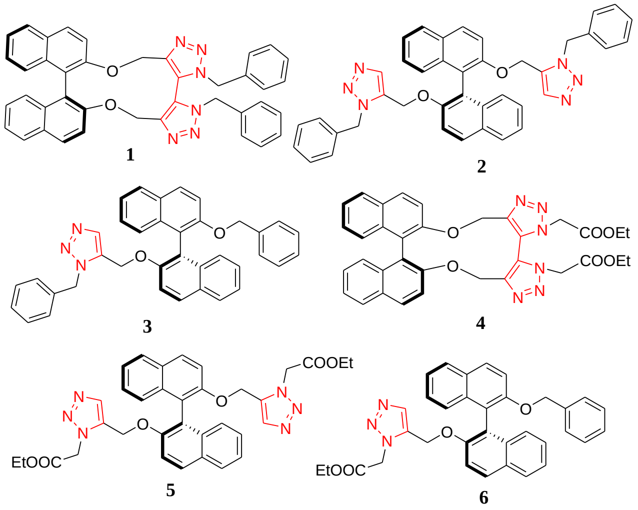
We have previously reported an interesting example of divergent catalysis with copper(I) catalyst controlled by amine-functional macromolecular polysiloxanes (Scheme 1).[8] In this work, we successfully demonstrated the interesting ability of the secondary amine-functional polysiloxane (**AFP-L2**) that led to oxidative coupling in the copper-mediated Huisgen reactions of general azides and alkynes with good yields and selectivities. Comparably, it is also surprising that the use of diamine-functional polysiloxane (**AFP-L1**) as a polymeric ligand led to classic Huisgen[3+2] -cycloaddition in excellent yields. However, the subsequent investigation of the catalytic application of these triazoles or bis-triazoles in homogeneous catalysis was not carried out. Inspired by previous reports on the organocatalyzed kinetic resolution/silylation of alcohols,[9] Herein, we began the study on the catalytic activity of various chiral triazoles in asymmetric silylation of alcohol.

The novel cyclic triazole dimer derivatives (Scheme 2) could be prepared from binaphthol (BINOL) according to previous reports,[8,10] in which the key step was the copper-promoted click reaction or the oxidative coupling from the dipropargyl and the substituted azide (See Supporting Information). The classic copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) of the monopropargyl compound and dipropargyl compound with azide, providing the desired mono- and di-click adducts (**3, 6** and **2, 5** respectively) in good yields. And the click reactions mediated by polysiloxane-supported secondary amine allow to the preparation of novel heterocyclic compounds, bistriazoles **1** and **4**. All these compounds **1-6** were characterized by NMR, HRMS and FTIR (Also see Supporting Information).



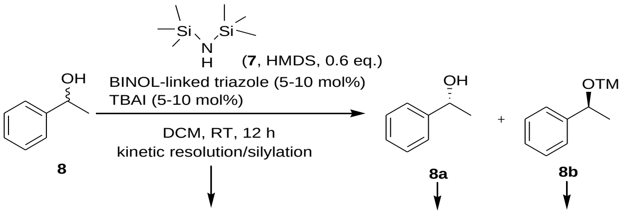
AFP-L1 (Si) = the secondary-primary diamine-functional polysiloxane
AFP-L2 (Si) = the secondary amine-functional polysiloxane

Scheme 1. Previous work: Divergent synthesis of triazoles[12]



Scheme 2. The cyclic and acyclic BINOL-based triazole derivatives.

Initially, we selected BINOL-linked triazoles **1** and **2** as model organocatalysts in the catalytic asymmetric kinetic resolution/silylation of 1-phenylethanol (**8**). As shown in Scheme 3, the promising results from the kinetic resolution/silylation of 1-phenylethanol with hexamethyldisilazane (HMDS) promoted by the BINOL-linked triazole (**1**) suggested that the Lewis basic triazole would prove to be viable organocatalyst in this reaction. Notably, enantiomeric excess of 1-phenylethanol was detected in the presence of catalytic amount of BINOL-linked triazole (Entry 1 of Scheme 3, 5% *ee* of **8a** by triazole **1**), while the combinational of TBAI with BINOL-linked triazole **1** or **2** led to poor conversion and no enantioselectivity (Entries 2, 4, and 6 of Scheme 3). Thus, the low reactivity of the BINOL-linked triazole and TBAI raised the concerns about the possibility of quenching of catalytic activity of BINOL-linked triazoles, in which the combined catalyst system might result in the formation of anion-π interactions of BINOL-linked triazole and TBAI. Inspired by previous work on anion-π interactions[11] and the above experimental results, we hypothesized that the possible anion-π interactions of BINOL-linked triazoles with TBAI would led to the establishment of BINOL-linked triazoles as an iodide ion sensor.



		8a	8b
1)	Only BINOL-linked triazole **1** (5 mol%):	52% yield 5% *ee*	48% yield
2)	TBAI and BINOL-linked triazole **1** (5 mol%):	no *ee*	<10% yield
3)	Only BINOL-linked triazole **2** (10 mol%):	no *ee*	18% yield
4)	TBAI and BINOL-linked triazole **2** (10 mol%):	no *ee*	<5% yield
5)	Only BINOL-linked triazole **1** (10 mol%):	no *ee*	93% yield
6)	TBAI and BINOL-linked triazole **1** (10 mol%):	no *ee*	<5% yield
7)	Only TBAI (10 mol%):	-	43% yield

Scheme 3. Kinetic resolution of 1-phenylethanol (**8**) with HMDS (**7**) by (*S*)-BINOL-linked triazole-promoted catalytic asymmetric silylation.

Notably, the substituted triazoles have been used as chemosensors for various cations and anions in the past years.[14-16] For example, the triazole based sensors are selective for Cu^{2+}, Hg^{2+}, Ag^{+}, Zn^{2+}, Fe^{3+} and Cd^{2+},[14] and few reports about the recognition of anions, such as Br^-, $HP_2O_7^{3-}$ and SO_4^{2-}.[15] However, although this electron-poor heterocycles can be readily synthesized, the triazole unit has remained ignored in the research field of fluorescent sensor, and accordingly the interaction between an anion and the electron-deficient triazole system have been neglected as a foothold for the construction of efficient anion receptors. In the past decades, the development of fluorogenic chemosensors for sensing anions selectively has attracted much attention because of the fundamental roles played by anions in a wide range of biological, chemical, and environmental processes.[17] Among the anions, the detection of iodide anion is of particular interest for its biological activities, such as neurological and thyroid functions.[18] However, only a few iodide anion sensors have been developed to date because of the lack of efficient receptors,[19] mainly ascribed to that the iodide anion is characteristic of large size, low charge density, and low hydrogen-bonding ability, thus the binding capacities of that with receptors are relatively weak. Therefore it remains a challenge to design chemosensors which can bind iodide selectively.

Notably, almost all the reported triazole anion receptors were based on hydrogen bonding and size selective.[20] At the same time, there is a growing interest in anion-π interactions, the non-covalent contacts between an anion and an electron deficient aromatic ring.[21] Till now, only Caballero and Molina reported that the bis(triazolium)-based receptor can recognize the hydrogenpyrophosphate anion based on anion-π interaction and hydrogen bonding.[22] Interestingly, there has been no report on selective detection of I^- based on click addition-generated triazoles so far.

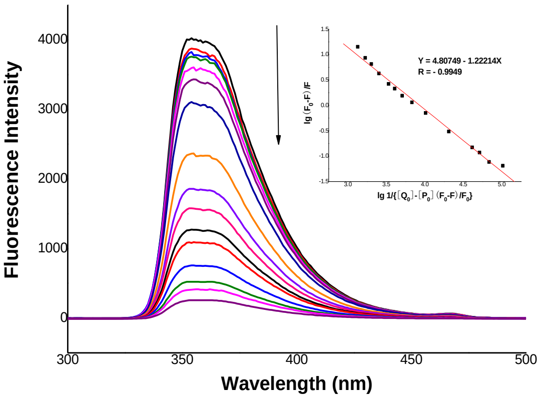


Figure 1. Fluorescence spectra of Ligand **1** (5 μM) in CH_3CN with increasing concentration of I-, Inset shows a Modified Stern-Volmer plot of Ligand **1** upon the addition of I^- in CH_3CN.

Initially, it was found that all the compounds in Scheme 2 gave strong fluorescent emission at 355-370 nm. The fluorescent titration of compound **1** with I^- anion (TBAI) was shown in Figure 1, where a notably fluorescence quenching at 355-367 nm was observed. The fluorescence intensity of **1** could be quenched almost 94% by the addition of 150 equiv of I^-. The efficiency of quenching was further studied by plotting a Modified Stern-Volmer plot as shown in the inset of Figure 1, and the fluorescent quenching coefficient K_{sv} is further calculated from the equation.[23]

$$\lg (F_0-F)/I = n \lg K_a - n \lg 1/\{[Q_0] - [P_0] (F_0 - F)/ F_0\}$$

where F_0 and F represent the fluorescence intensity in the absence and presence of I^-, respectively, $[Q_0]$ is the molar concentration of the quencher I^-, and $[P_0]$ is the molar concentration of the ligand. K_{sv} is the quenching constant, and n is the ratio between iodide and the ligand. From the Stern-Volmer plot, the K_{sv} and n are calculated as 8.6×10^3 and 1.22, respectively for ligand **1**, while for the compound **4**, the K_{sv} and n are 9.4×10^3 and 1.06 (Table 1), which indicate the promising anion binding affinities exist possibly due to the anion-π interaction between I^- and the electron-deficient triazole ring system. From Table 1, it is clear that the K_{sv} of CH_2COOEt-substituted ligands **4** and **6** are higher than that of the corresponding CH_2Ph-substituted **2** or **3**. This is possibly due to the electron withdrawing ability of the

CH_2COOEt-substituted ligands **4** or **6** can enhance the electron withdrawing character of the triazole ring, then strengthen the binding affinities between I^- and the triazole unite. The quenching mechanism can be explained by the heavy-atom effect, e.g. from the formation of a charge-transfer-complex as discussed above, the "heavy-atom" interaction between the ground state of the triazole containing complex and the inorganic anion (iodide) leads to an enhancement of the spin-orbit coupling and thus the associated fluorescence quenching.[24]

Table 1. Quenching constants K_{sv} and binding sites n from the titration of Ligand **1-6** with TBAI.

Ligand	K_{sv} (mol^{-1})	n	r
1	8.6×10^3	1.22	-0.995
2	5.5×10^3	1.30	-0.996
3	7.1×10^3	1.22	-0.995
4	9.4×10^3	1.06	-0.972
5	7.5×10^3	1.09	-0.978
6	8.3×10^3	1.04	-0.980

r is the regression coefficient.

As shown in Figure 2, the UV-vis spectra showed a broad absorption band centered at 234 nm. For compound **2**, **3**, **4**, **5** and **6**, the absorption maxima were all observed at 231 nm. Titration of all the ligands with I^- were also monitored via UV-vis spectroscopy. Upon addition of I^-, the compounds all showed a slight red shift of 13-15 nm. The red shift in the absorption can be explained by the formation of the charge-transfer-complex between the donor (I^-) and the π acceptor (the triazole ring). At the same time, a new peak was observed improving at 212 nm upon the continuous addition of TBAI, which may be ascribed to the interaction of the iodide with the triazole ring.

The ^{1}H-NMR spectrum of the compound **6** (Figure 3), displays mainly four sets of signals; the first characteristic set of signals is ascribed to the naphthalene protons, which appeared at δ = 7.94, 7.88, 7.46, 7.34 and 7.22 ppm respectively. The second of them is appear as a multiplets at δ = 7.13 ppm and a doublets at δ = 6.87 ppm due to the phenyl protons. The *-CH* proton of the triazole ring appears as a singlet at δ = 6.77 ppm. Finally, the three different of AB-quartet pattern protons from ArO-CH_2- and -CH_2-COOEt appear at δ = 5.26, 5.04 and 4.65 ppm respectively. With addition of 10 equiv of TBAI to the compound **1-6** in $CDCl_3$, the solution color gradually turned from colorless to pale green, which indicates the formation of anion-π interaction complex.

Figure 3 further depicts the ^{1}HNMR spectra of compound **6** after the addition of TBAI. Obviously, all of the signals were up-field shifted. These agree well with the formation of **6**-I complex: (1) the complexation with I^- will weaken the electron-withdrawing character of the triazole ring and as a result the HNMR signals of triazole-CH_2 (three AB quartet) are up-field shifted ($\Delta\delta$ = -0.094, -0.065 and -0.050 ppm). (2) the interaction with I^- will enhance the π electron density of the naphthalene and phenyl ring, which caused the corresponding protons up-field shift. ($\Delta\delta$ = -0.067, -0.069, -0.069 etc for naphthalene, $\Delta\delta$ = -0.076, -0.076 ppm for phenyl). (3) In contrast, the triazole C-H only show a small *up*-field shift ($\Delta\delta$ = -0.040), apparently the C-H bonds play little role in recognition, e.g. there is almost no hydrogen bonding exist in the sensing process. Thus the spectra analysis, including UV and NMR titration, demonstrated that anion-π interaction of I^- to the triazole ring was an indirect evidence to the deactivation in the catalytic silylation of alcohol with HMDS.

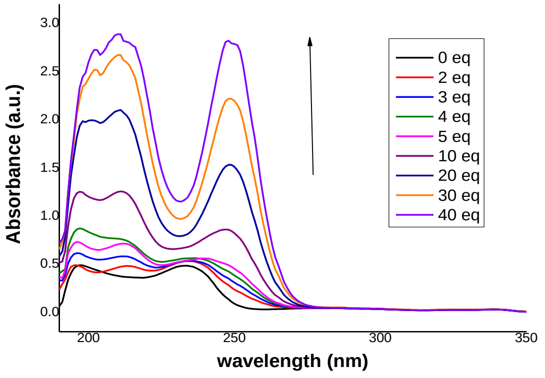


Figure 2. UV-Vis titration spectra of Ligand **1** (5 μM) in CH_3CN with increasing concentration of I^- in CH_3CN.

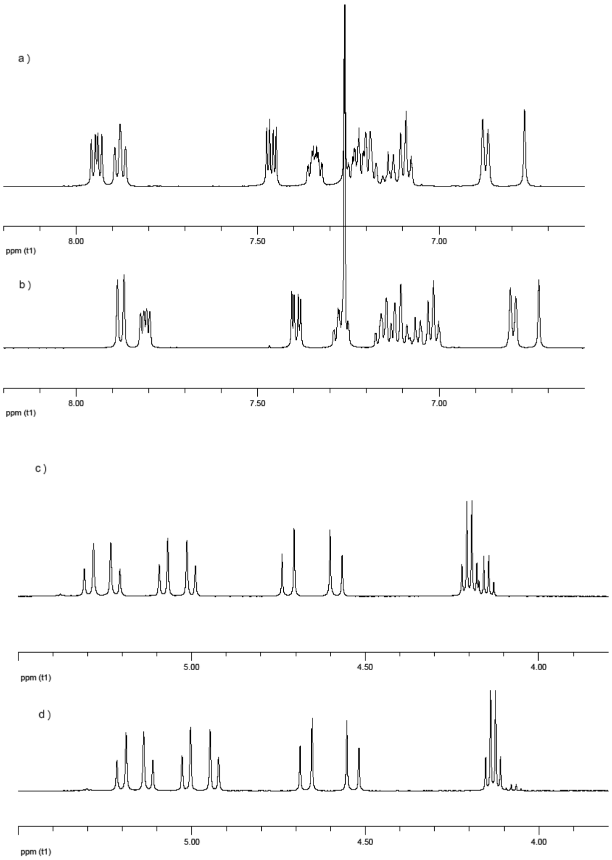
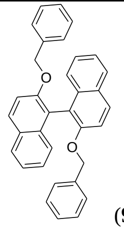
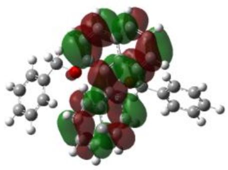
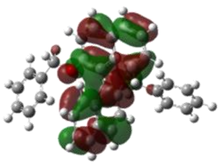
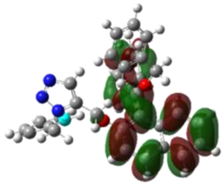
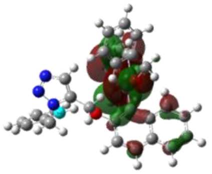
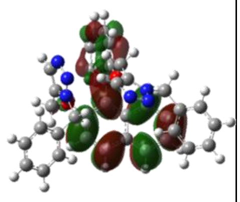
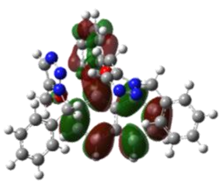
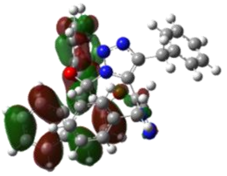
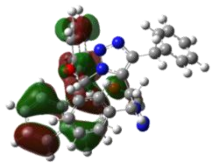


Figure 3. ^{1}HNMR spectrum (500 MHz, $CDCl_3$) of Ligand **6** before (a), (c) and after addition of 10 equiv of I^- (b), (d).

To obtain a better understanding of the observed florescent properties and molecule recognition with iodide, theoretical calculations were performed using Gaussian 09 software package[25]. The electron density diagrams for HOMO and LUMO orbitals of BINOL-derived triazoles **1**~**3** as well as the BINOL-derived ether **9** (Φ_F = 0.15) that exhibited poor selectivity for iodide.[26] Notably, the Φ_F values of **1**, **2**, **3**, **4**, **5**, **6** are 0.40, 0.47, 0.66, 0.60, 0.55 and 0.49 respectively. It is noteworthy that the electron density of both HOMO and LUMO of these compounds is predominantly distributed along the binaphthyl unit. However, for BINOL-derived triazole **3** containing a benzyl group and a triazole, HOMO level has the charge localized on the benzyl ring while LUMO level has distributed along the naphthyl ring that linked with benzyl ether. This feature indicates that the energies of orbitals could be affected by triazole and benzyl unit. These electronic effects and fluorescent analysis/molecule recognition of the BINOL-derived triazoles would be beneficial to the molecular design of task-directed fluorescent sensor in the near future.

Table 2. Frontier orbital shape and energy (in eV) calculated at B3LYP/6-31G(d,p) level of theory[15]

	LUMO(eV)	HOMO(eV)
 **(9)** $\Phi_F = 0.15$		
	-0.939	-5.289
BINOL-derived triazole 3 (*see* Scheme 2) Φ_F = 0. 66		
	-1.180	-5.610
BINOL-derived triazole 2 (*see* Scheme 2) $\Phi_F = 0.47$		
	-1.310	-5.581
BINOL-derived triazole 1 (*see* Scheme 2) $\Phi_F = 0.40$		
	-1.091	-5.547

Conclusions

In summary, a compelling experimental evidence for the existence of anion-π interactions in this molecular recognition system is provided directly by the model kinetic resolution/silylation of 1-phenylethanol with hexamethyldisilazane. With or without the addition of TBAI, the catalytic activity of BINOL-linked triazoles varied dramatically due to the contributions from anion-π interactions. On the basis of catalytic activity of BINOL-linked triazoles in asymmetric silylation of alcohol, we have discovered firstly that a new type of fluorescent sensor with cyclic or acyclic BINOL skeleton containing triazole groups, showed high fluorescence emission and high selective recognition for iodide. The spectra analysis, including UV and NMR titration, demonstrated that anion-π interaction between I^- and the triazole ring was responsible for the formation of weakly charge-transfer-complex. In other words, we have demonstrated the ability of BINOL-derived triazoles as sensors to detect iodide ions in solution and the fluorescence almost completely quenched by heavy-atom effect. This fluorescence recognition of I^- possess the following features: (1) The sensing process are constructed on the anion-π interaction between the I^- donor and the electron deficient triazole ring. (2) All the BINOL-derived triazole sensors **1-6** exhibit good selectivity toward I^-, which supported the triazole unite is a promising backbone in the molecular design of fluorescent sensor for selective interaction with iodide. Thus the new chemistry in this manuscript was catalysis –initiated fluorescent analysis, which would be an attractive concept in the analytic chemistry. Undoubtedly, evidence that triazole-containing BINOL-derived sensors have the functionality of anion-π recognition may contribute to metal-free organocatalysis in the near future and opens new perspectives for the construction of supramolecular complexes with anions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ J. F. Zou and C. Y. Wang contributed equally to this work.

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