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Synthesis and Characterization of Bis-*N*-2-Aryl Triazole as a Fluorophore

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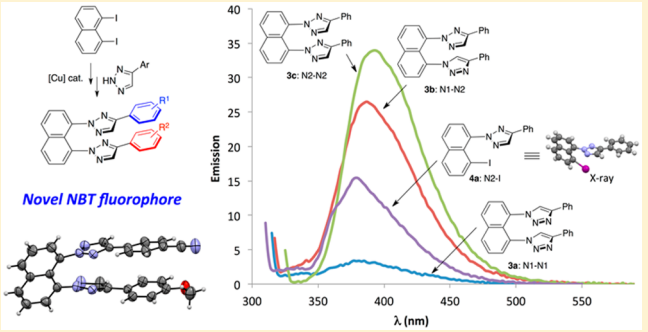
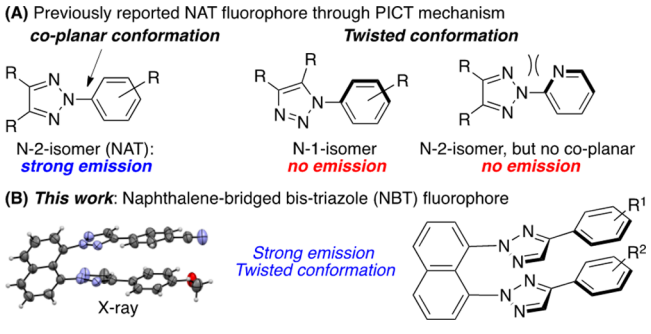
Supporting Information

ABSTRACT: Naphthalene-bridged bis-triazole (NBT) complexes were prepared and characterized for investigation of their photophysical properties. Unlike our previously reported *N*-2-aryl triazoles, which gave strong emissions through the planar intramolecular charge transfer mechanism (coplanar conformation), this newly developed NBT adopted a non-coplanar conformation between triazole and naphthalene, achieving fluorescence through twisted intramolecular charge transfer.



Small organic molecules that can provide strong fluorescence emissions are of great importance to the scientific community.[1] These molecular fluorophores have been applied to a wide range of research areas, including chemistry, biology, and material science.[2] In 2011, our group reported *N*-2-aryl-1,2,3-triazoles (NAT) as novel fluorophores with strong emission in the high-energy UV/blue region.[3] The experimental results (X-ray structures) and computational studies confirmed the coplanar conformation (observed in N-2 isomers, Scheme 1A) as the key factor for fluorescence emission. On the basis of these studies, planar intramolecular charge transfer (PICT) was proposed as a plausible mechanism for the observed excellent optical properties of this novel NAT system. Herein, we report the design and synthesis of naphthalene-bridged bis-triazole (NBT) compounds, which give excellent fluorescence emissions, even with a twisted conformation between triazole and the N-2 aryl groups (Scheme 1B), suggesting twisted intramolecular charge transfer (TICT) is a plausible mechanism for the observed strong fluorescence emission.[4]

Scheme 1. *N*-2-Aryl Triazole Fluorophores



We have previously reported that *N*-2-aryl triazole **1a** gave very strong fluorescence emission, whereas its N-1 isomer **1b** gave no emission at all. Two key factors appeared to control the fluorescence emission in these NAT dyes: N-2 substitution and coplanar conformation between the two rings. However, the second assumption was greatly challenged by our recent studies of *N*-naphthalene triazoles. As shown in Figure 1, we recently prepared *N*-naphthalene triazole **1c** (N-2 isomer) and **1d** (N-1

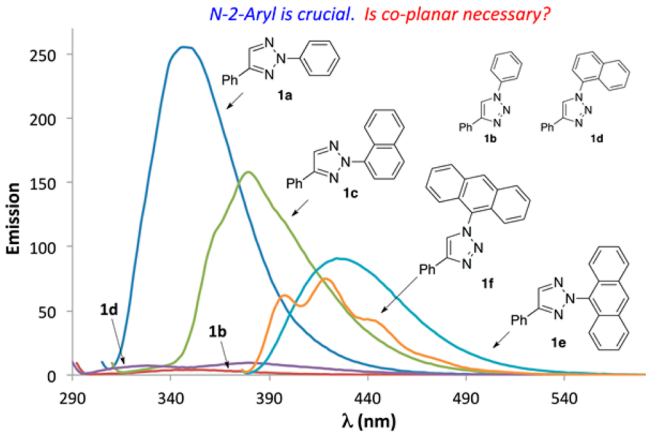


Figure 1. Fluorescence emission of NAT with different aryl groups.

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isomer). Similar to phenyl triazoles, N-1 isomer **1d** gave no fluorescence emission, and the N-2 isomer **1c** gave strong emission. However, a closer look at **1c** suggests that coplanar conformation between naphthalene and the triazole ring is highly unlikely due to steric repulsion. In fact, the crystal structure of a similar analogue indicated a 49.5° dihedral angle between the two rings in the N-2 isomer.[5] These results piqued our interest in further exploring this new class of dyes by questioning whether the coplanar conformation is necessary.[6]

Besides coplanar intramolecular charge transfer (PICT), another feasible photochemical process associated with this type of extended aromatic ring, twisted intramolecular charge transfer (TICT), was first introduced by Grabowski and co-workers.[7] One important feature of the TICT type of emission is the feasibility of the donor unit in initiating the charge transfer. A number of nitrogen-containing heterocycles have been studied as donors in TICT-emitting molecules.[8] However, to the best of our knowledge, 1,2,3-triazoles have never been used as a potential donor in TICT fluorophores, and their photochemical properties are unknown.

To explore triazole derivatives as potential TICT-emitting dyes, we prepared anthracene-substituted triazole **1e** (N-2) and **1f** (N-1). Clearly, the anthracene should provide a large enough steric repulsion to prevent formation of the coplanar conformation even in the N-2 isomer **1e**. Thus, the fluorescence emission should be mainly from the twisted state. Interestingly, both N-1 and N-2 isomers gave good emissions. However, three different emission bands were observed in N-1 isomer **1f**, which was similar to the typical emission of aromatic-substituted anthracene.[9] This result suggested that triazole-anthracene compounds were not good model molecules to access the triazole's influence on TICT emission due to the notable background emission from anthracene. To better evaluate the triazole influence in the twisted systems, we designed naphthalene-bridged bis-triazole (NBT).

As shown in Figure 2, bis-triazole can be readily prepared from copper-catalyzed coupling between naphthalene di-iodide

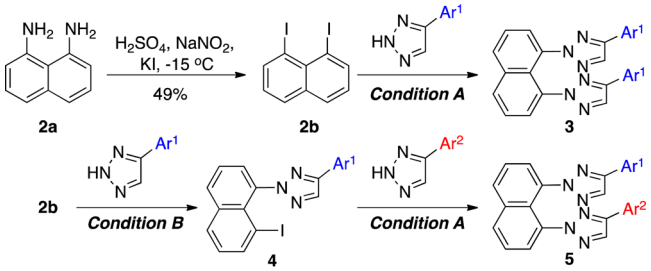

Figure 2. Synthesis of naphthalene-bridged bis-triazole (NBT).

2b and NH-triazole. Two different conditions were developed to reach NBT, either in a one-pot fashion (condition A) or a stepwise process (condition B).[5] Using these methods, both symmetrical NBT **3** and unsymmetrical NBT **5** could be easily prepared. Notably, both N-1 and N-2 isomers were observed in all cases. The regioselectivity (ratio between N-2 and N-1 isomers) depends on the substituted groups (Ar) similar to what has been observed previously in triazole functionalization.[10] The N-1 and N-2 isomers could be easily separated using column chromatography due to the significant polarity difference. Perhaps the most important question for the synthesis of NBT was how to identify the relative position of the two triazole rings with restricted rotation. Considering the rotation of C−N bonds, theoretically two conformers (cis and trans) could be formed. Interestingly, during our synthesis, only one conformer was observed in almost all cases, which was later confirmed as the cis-conformer via X-ray crystallography (Figure 3).

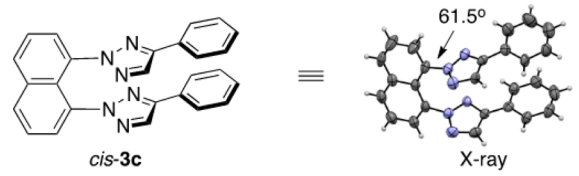

Figure 3. X-ray crystallography confirmed the formation of the cis-conformer.

As shown in the X-ray crystal structure, the twisted conformation was confirmed between the triazole and naphthalene rings with a dihedral angle of 61.5°. The crystal structure of mono-triazole-substituted **4a** (Ar1 = Ph, with I on naphthalene ring) was also obtained (see the Supporting Information (SI)). Similarly, according to this crystal structure, the dihedral angle between these two rings is 62.9°. With all of the NBTs clearly characterized, their fluorescent properties were measured and shown in Figure 4.

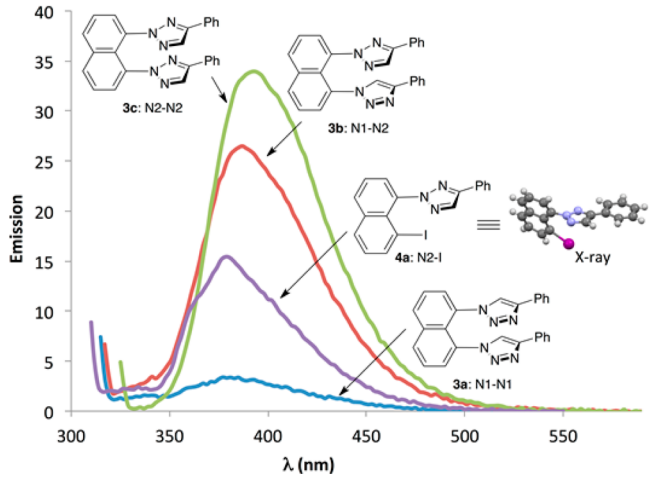

Figure 4. Fluorescence emission of NBT **3** and **4a**.

As shown by the crystal structures, both bis-triazole NBT **3** and mono-triazole **4** adopted a twisted conformation. However, whereas N-2 isomers generally gave good fluorescence emission, the N-1 isomers gave almost no emission in all cases. The emission intensity of NBT **3** followed a clear trend in that N2−N2 > N2−N1 > N1−N1 (almost no emission). Because of the rotation strain, it is impossible for NBT **3** to adopt planar conformation even in solution. Thus, the observed good fluorescence emission of the N-2 isomers likely represents the photochemical process associated with TICT states. The optical properties (emission, excitation, and quantum yields) of compounds **3** and **4** were determined and summarized in Table 1.

These N-2 isomers of NBTs were identified as a new class of fluorophores, and one interesting feature offered by the

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Table 1. Comparison of Optical Properties of Different NBTs[a]

	R^1/R^2	excitation (λ_{max})	emission (λ_{max})	Φ	Stokes shift (nm)
NAT					
1a		298	347	0.34	49
4a	N2-TA-I	300	378	0.20	78
NBT					
3a	$R^1 = R^2$ = H (N1−N1)			<0.01	
3b	$R^1 = R^2$ = H (N1−N2)	307	384	0.13	77
3c	$R^1 = R^2$ = H (N2−N2)	315	393	0.24	78
5a	$R^1 = R^2$ = Cl	305	393	0.26	88
5b	$R^1 = R^2$ = OMe	315	403	0.29	88
5c	$R^1 = R^2$ = COOMe	300	396	0.41	96
5d	$R^1 = R^2$ = CN	302	403	0.47	101
5e	R^1 = OMe, R^2 = CN	300	408	0.39	108

[a]Sample information: 1.0×10^{-6} mol/L in dichloromethane. Quantum yields (Φ) were determined based on 1.0×10^{-6} mol/L 9,10-diphenylanthracene in cyclohexane (Φ = 0.9). Photo emission integration calculated from the original spectra. All fluorescence was measured under identical conditions (see the SI).

naphthalene-bridge was the potential π-π stacking between the two triazoles.[11] As revealed by the X-ray structures, the two triazoles in NBT are almost parallel with a distance that is just slightly longer than van der Waals radii (see the space filling model in the SI). Thus, it is reasonable to expect that the substituted groups on the triazole phenyl ring may provide various electronic effects that will influence the overall optical properties.[3,12] To explore the substituted group influence, we prepared a series of symmetrical and unsymmetrical NBTs **5a**−**e** with various substituents on the triazole phenyl rings. Their photochemical properties were evaluated (Table 1), and the spectra of some representative NBTs are shown in Figure 5.

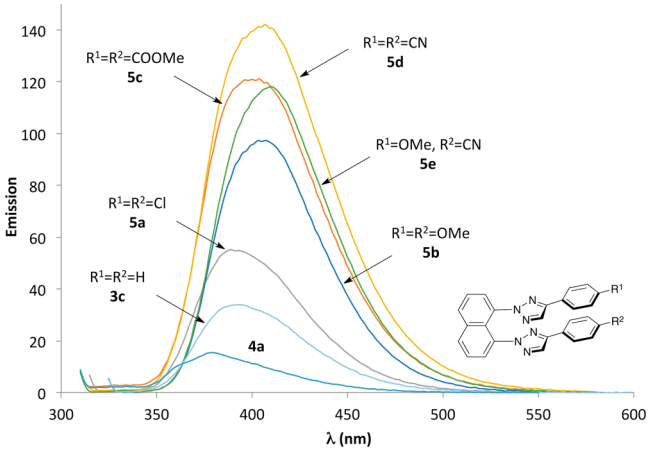

Figure 5. Fluorescence emission of NBT **5** and **4a**.

Among all the tested NBTs, N-2 substitution is crucial for effective emission. Compared with previous planar NAT **1a**, the new twisted NBT fluorophores give more red shifted emissions around 400 nm (blue light). Interestingly, although the two triazole rings are almost parallel, changing the substituent groups on the phenyl rings did not influence the overall emission of the NBT. For example, with either EDG (**5b**)- or EWG (**5c** and **5d**)-substituted NBT, there were little changes in the emission and excitation wavelengths. Furthermore, substrate **5e**, with EDG and EWG incorporated on different rings, also gave similar emission, which strongly suggested that little π-π interactions occurred between the two rings. Notably, the substituent group did help to improve the quantum yields (up to 47%) through the introduction of extended conjugations.[13] Overall, compared with NAT, this new NBT system gave significantly higher fluorescence efficiency, which implies great potential for future applications.

In conclusion, we report a new type of triazole-based fluorescence-active compound: naphthalene-bridged bis-triazole (NBT). Practical syntheses have been developed, and regio-isomers of compounds have been characterized by X-ray crystallography. The fluorescence studies reveal that in this twisted system, N-2 substitution is crucial for fluorescence emission. Compared to the previously reported NAT system, this new NBT gives higher fluorescence efficiency and larger Stokes shifts, which warrants the new molecule as a potential fluorophore for chemical and biological applications.

EXPERIMENTAL SECTION

General Information. All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from commercial providers and used without further purification. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.0 ppm) or *d*6-DMSO (δ 39.5 ppm) for ^{13}C NMR.

Representative Procedure for the Preparation of 2-(Anthracen-9-yl)-4-phenyl-2*H*-1,2,3-triazole (1e) (Condition A). To a solution of 9-bromoanthracene (514 mg, 2.0 mmol, 1.0 equiv) in dry DMSO (4 mL, 0.5 M) were successively added 4-phenyl-1,2,3-NH-triazole (725 mg, 5.0 mmol, 2.5 equiv), CuI (76 mg, 20%), L-proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 equiv) under a N_2 atmosphere. The mixture was stirred at 120 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v 20:1), giving the desired product as a yellow solid (yield: 340 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.37 (s, 1H), 8.32 (dd, *J* = 5.8, 3.3 Hz, 1H), 8.09 (dd, *J* = 7.1, 1.9 Hz, 2H), 8.00−7.98 (m, 2H), 7.79 (dd, *J* = 5.8, 3.3 Hz, 1H), 7.51−7.44 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.94, 134.1, 132.5, 131.3, 129.5, 129.00, 128.85, 128.70, 128.2, 127.6, 127.2, 126.2, 125.7, 122.6. HRMS: $[M + H]^+$ calcd for $C_{22}H_{15}N_3$, 322.1338; found, 322.1342.

Representative Procedure for the Preparation of 1-(Anthracen-9-yl)-4-phenyl-1*H*-1,2,3-triazole (1f) (Condition A). To a solution of 9-bromoanthracene (514 mg, 2.0 mmol, 1.0 equiv) in dry DMSO (4 mL, 0.5 M) were successively added 4-phenyl-1,2,3-NH-triazole (725 mg, 5.0 mmol, 2.5 equiv), CuI (76 mg, 20%), L-

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proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 equiv) under a N_2 atmosphere. The mixture was stirred at 120 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v 15:1), giving the desired product as a light yellow solid (yield: 237 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.20 (s, 1H), 8.11 (d, J = 7.6 Hz, 2H), 8.03 (d, J = 8.4 Hz, 2H), 7.55−7.51 (m, 5H), 7.43−7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 131.2, 130.3, 129.8, 129.0, 128.46, 128.35, 128.0, 127.4, 126.7, 125.97, 125.89, 124.0, 122.1. HRMS: $[M + H]^+$ calcd for $C_{22}H_{15}N_3$, 322.1338; found, 322.1342.

Representative Procedure for the Preparation of 1,8-Bis(4-phenyl-2*H*-1,2,3-triazol-2-yl)naphthalene (3c) (Condition A). To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 equiv) in dry DMSO (4 mL, 0.5 M) were successively added 4-phenyl-1,2,3-NH-triazole (725 mg, 5.0 mmol, 2.5 equiv), CuI (76 mg, 20%), L-proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 equiv) under a N_2 atmosphere. The mixture was stirred at 120 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v 5:1), giving the desired product as a light yellow solid (yield: 472 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, J = 8.4, 1.2 Hz, 2H), 7.96 (dd, J = 7.4, 1.2 Hz, 2H), 7.71 (dd, J = 8.2, 7.4 Hz, 2H), 7.48−7.51 (m, 4H), 7.28−7.22 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 136.1, 135.6, 131.7, 130.2, 129.4, 128.5, 128.3, 127.0, 125.9, 121.1. HRMS: $[M + H]^+$ calcd for $C_{26}H_{18}N_6$, 415.1666; found, 415,1672.

Representative Procedure for the Preparation of 2-(8-Iodonaphthalen-1-yl)-4-phenyl-2*H*-1,2,3-triazole (4a) (Condition B). To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 equiv) in dry DMSO (4 mL, 0.5 M) were successively added 4-phenyl-1,2,3-NH-triazole (290 mg, 2.0 mmol, 1.0 equiv), CuI (38 mg, 10%), L-proline (46 mg, 20%), and K_2CO_3 (552 mg, 4.0 mmol, 2.0 equiv) under a N_2 atmosphere. The mixture was stirred at 80 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v 10:1), giving the desired product as a light yellow solid (yield: 401 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (dd, J = 7.4, 1.2 Hz, 1H), 8.21 (s, 1H), 8.04 (dd, J = 8.3, 1.3 Hz, 1H), 7.97 (dd, J = 8.3, 1.1 Hz, 1H), 7.94−7.91 (m, 2H), 7.68 (dd, J = 7.2, 1.6 Hz, 1H), 7.59 (dd, J = 8.1, 7.3 Hz, 1H), 7.49−7.45 (m, 2H), 7.42−7.38 (m, 1H), 7.19 (dd, J = 8.1, 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 143.0, 137.2, 135.8, 132.6, 132.0, 130.1, 129.5, 129.1, 128.92, 128.75, 128.73, 127.4, 126.2, 125.2, 86.5. HRMS: $[M + H]^+$ calcd for $C_{18}H_{22}N_3I$, 398.0149; found, 398.0155.

Representative Procedure for the Preparation of 1,8-Bis(4-phenyl-1*H*-1,2,3-triazol-1-yl)naphthalene (3a). To a solution of 1,8-diazidonaphthalene (420 mg, 2.0 mmol, 1.0 equiv) in 1:1 *t*-BuOH/H_2O (5 mL, 0.4 M) were successively added phenylacetylene (1.02 g, 10.0 mmol, 5.0 equiv), $CuSO_4$ (128 mg, 40%), and L-ascorbic acid sodium salt (237.6 mg, 60%) under a N_2 atmosphere. The mixture was stirred at 80 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v 5:1), giving the desired product as a light yellow solid (yield: 712 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (dd, J = 8.3, 1.2 Hz, 1H), 7.75 (t, J = 7.8 Hz, 1H), 7.66 (dd, J = 7.6, 1.2 Hz, 1H), 7.56 (s, 1H), 7.47−7.43 (m, 2H), 7.25−7.21 (m, 3H). ^{13}C NMR (100 MHz, *d*6-DMSO): δ 146.4, 135.7, 132.1, 131.7, 130.5, 129.4, 128.7, 128.0, 127.0, 125.8, 124.4. HRMS: $[M + H]^+$ calcd for $C_{26}H_{18}N_6$, 415.1665; found, 415.1677.

Representative Procedure for the Preparation of 2,3′-(Naphthalene-1,8-diyl)bis(5-phenyl-2*H*-1,2,3-triazole) (3b). 2-(8-azidonaphthalen-1-yl)-4-phenyl-2*H*-1,2,3-triazole was prepared from 1-azido-8-iodonaphthalene under condition B. Then, to a solution of 2-(8-azidonaphthalen-1-yl)-4-phenyl-2*H*-1,2,3-triazole (624 mg, 2.0 mmol, 1.0 equiv) in 1:1 *t*-BuOH/H_2O (5 mL, 0.4 M) were successively added phenylacetylene (510 mg, 5.0 mmol, 2.5 equiv), $CuSO_4$ (64 mg, 20%), and L-ascorbic acid sodium salt (118.8 mg, 30%) under a N_2 atmosphere. The mixture was stirred at 120 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v 3:1), giving the desired product as a light yellow solid (yield: 605 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, J = 7.5, 5.2 Hz, 2H), 7.84 (d, J = 7.2 Hz, 1H), 7.79 (d, J = 7.1 Hz, 1H), 7.72 (t, J = 7.8 Hz, 2H), 7.63 (s, 1H), 7.52 (s, 1H), 7.45 (ddd, J = 12.2, 6.4, 2.7 Hz, 4H), 7.26−7.24 (t, J = 3.0 Hz 3H), 7.18 (t, J = 2.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 146.9, 135.8, 135.0, 132.4, 132.0, 131.1, 130.8, 129.7, 129.1, 128.52, 128.48, 128.38, 128.25, 128.08, 127.7, 126.16, 126.12, 126.04, 125.5, 122.3, 121.6, 116.0. HRMS: $[M + H]^+$ calcd for $C_{26}H_{18}N_6$, 415.1665; found, 415.1672.

Representative Procedure for the Preparation of 1,8-Bis(4-(4-chlorophenyl)-2*H*-1,2,3-triazol-2-yl)naphthalene (5a) (Condition A). To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 equiv) in dry DMSO (4 mL, 0.5 M) were successively added 4-(4-chlorophenyl)-1,2,3-NH-triazole (898 mg, 5.0 mmol, 2.5 equiv), CuI (76 mg, 20%), L-proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 equiv) under a N_2 atmosphere. The mixture was stirred at 120 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v 5:1), giving the desired product as a light yellow solid (yield: 580 mg, 60%). ^{1}H NMR (400 MHz, $CDCl^3$): δ 8.14 (dd, J = 8.4, 1.1 Hz, 2H), 7.95 (dd, J = 7.4, 1.2 Hz, 2H), 7.72 (dd, J = 8.1, 7.6 Hz, 2H), 7.56 (s, 2H), 7.42−7.39 (m, 4H), 7.24−7.22 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 136.0, 135.3, 134.3, 131.44, 131.41, 130.4, 128.7, 127.8, 127.07, 127.00, 126.0, 121.0. HRMS: $[M + H]^+$ calcd for $C_{26}H_{16}N_6Cl_2$, 483.0887; found, 483.0897.

Representative Procedure for the Preparation of 1,8-Bis(4-(4-methoxyphenyl)-2*H*-1,2,3-triazol-2-yl)naphthalene (5b) (Condition A). To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 equiv) in dry DMSO (4 mL, 0.5 M) were successively added 4-(4-methoxyphenyl)-1,2,3-NH-triazole (875 mg, 5.0 mmol, 2.5 equiv), CuI (76 mg, 20%), L-proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 equiv) under a N_2 atmosphere. The mixture was stirred at 120 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v 5:1), giving the desired product as a light yellow solid (yield: 607 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (dd, J = 8.4, 1.2 Hz, 2H), 7.94 (dd, J = 7.4, 1.2 Hz, 2H), 7.69 (dd, J = 8.2, 7.4 Hz, 2H), 7.50 (s, 2H), 7.44−7.40 (m, 4H), 6.80−6.76 (m, 4H), 3.80 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 148.0, 136.0, 135.6, 131.1, 130.0, 127.2, 126.9, 125.9, 122.2, 121.2, 113.8, 55.1. HRMS: $[M + H]^+$ calcd for $C_{28}H_{22}N_6O_2$, 475.1877; found, 475.1883.

Representative Procedure for the Preparation of Dimethyl 4,4′-(2,2′-(Naphthalene-1,8-diyl)bis(2*H*-1,2,3-triazole-4,2-diyl))dibenzoate (5c) (Condition A). To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 equiv) in dry DMSO (4 mL, 0.5 M) were successively added 4-(1*H*-1,2,3-triazole-4-yl)-benzoic acid methyl ester (1.015 g, 5.0 mmol, 2.5 equiv), CuI (76 mg, 20%), L-proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 equiv) under a N_2 atmosphere. The mixture was stirred at 120 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v

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5:1), giving the desired product as a light yellow solid (yield: 456 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 7.4 Hz, 2H), 7.86 (d, J = 8.2 Hz, 4H), 7.73 (t, J = 7.8 Hz, 2H), 7.62 (s, 2H), 7.51 (d, J = 8.3 Hz, 4H), 3.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 147.2, 136.0, 135.2, 133.5, 132.01, 131.96, 130.5, 129.82, 129.69, 127.2, 126.0, 125.5, 121.0, 52.1. HRMS: [M + Na]$^+$ calcd for $C_{30}H_{22}N_6O_4$, 553.1595; found, 553.1600.

Representative Procedure for the Preparation of 4,4′-(2,2′-(Naphthalene-1,8-diyl)bis(2*H*-1,2,3-triazole-4,2-diyl))-dibenzonitrile (5d) (Condition A). To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 equiv) in dry DMSO (4 mL, 0.5 M) were successively added 4-(2*H*-1,2,3-triazol-4-yl)-benzonitrile (850 mg, 5.0 mmol, 2.5 equiv), CuI (76 mg, 20%), L-proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 equiv) under a N_2 atmosphere. The mixture was stirred at 120 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v 5:1), giving the desired product as a light yellow solid (yield: 389 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 7.4 Hz, 2H), 7.76 (dd, J = 9.7, 6.0 Hz, 2H), 7.63 (s, 2H), 7.63–7.53 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 136.0, 135.0, 133.5, 132.4, 131.9, 130.7, 128.4, 127.1, 126.1, 120.7, 118.3, 112.0. HRMS: [M + Na]$^+$ calcd for $C_{28}H_{16}N_8$, 487.1390; found, 487.1396.

Representative Procedure for the Preparation of 5e (Conditions A and B). To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 equiv) in dry DMSO (4 mL, 0.5 M) were successively added 4-(4-methoxyphenyl)-1,2,3-NH-triazole (350 mg, 2.0 mmol, 1.0 equiv), CuI (38 mg, 10%), L-proline (46 mg, 20%), K_2CO_3 (552 mg, 4.0 mmol, 2.0 equiv) under a N_2 atmosphere. The mixture was stirred at 80 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v 10:1), giving the desired intermediate 2-(8-iodonaphthalen-1-yl)-4-(4-methoxyphenyl)-2*H*-1,2,3-triazole as a light yellow solid (yield: 563 mg, 66%). To the solution of 2-(8-iodonaphthalen-1-yl)-4-(4-methoxyphenyl)-2*H*-1,2,3-triazole (854 mg, 2.0 mmol, 1.0 equiv) in dry DMSO (4 mL, 0.5 M) were successively added 4-(2*H*-1,2,3-triazol-4-yl)-benzonitrile (850 mg, 5.0 mmol, 2.5 equiv), CuI (76 mg, 20%), L-proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 equiv) under a N_2 atmosphere. The mixture was stirred at 120 °C and monitored by TLC. After the reaction was completed, it was quenched with brine and extracted with ethyl acetate three times. The organic phases were combined, and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (hexane/EtOAc v/v 5:1), giving the desired product as a light yellow solid (yield: 498 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16–8.12 (m, 2H), 7.96–7.94 (m, 2H), 7.73 (ddd, J = 8.3, 7.4, 1.0 Hz, 2H), 7.65 (s, 1H), 7.59–7.57 (m, 2H), 7.52–7.49 (m, 3H), 7.39–7.37 (m, 2H), 6.77–6.75 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 148.1, 146.3, 136.0, 135.39, 135.24, 133.9, 132.3, 132.05, 132.01, 131.05, 131.01, 130.6, 130.2, 127.13, 127.05, 126.27, 126.11, 125.9, 121.8, 121.0, 118.6, 113.9, 111.5, 55.28. HRMS: [M + Na]$^+$ calcd for $C_{28}H_{19}N_7O$, 492.1543; found, 492.1550.

UV Absorption Spectra. The UV–Vis spectra were measured in 10.00 mm quartz cells. All samples were measured as 10^{-6} mol/L solutions of bis-*N*-2-aryl triazole in CH_2Cl_2. The wavelength range is between 200 and 600 nm.

Fluorescence Excitation and Emission Spectra. Fluorescence emission and excitation spectra were measured in 10.00 mm quartz cells. All samples were measured as 10^{-6} mol/L solutions of bis-*N*-2-aryl triazole in CH_2Cl_2. The emission spectra were obtained with an excitation wavelength around 300 to 310 nm, and the excitation spectra were obtained with emission λ_{max} according to different compounds.

Quantum Yields. Quantum yields were calculated using the standard 9,10-diphenylanthracene, which excited at 340 nm (Φ = 0.9) in cyclohexane. Quantum yields were calculated using the following equation, where Φ is the quantum yield, Int is the area of the emission peak, A represents absorbance at the excitation wavelength, and n is the reflective index of the solvent. The subscript reference is the respective values of the standard 9,10-diphenylanthracene. The absorptions of bis-*N*-2-aryl triazole and 9,10-diphenylanthracene were <0.05 (concentrations = 10^{-6} mol/L).

$$\phi = \phi_{reference} \times \frac{Int \times A_{reference \times n^2}}{Int \times A \times n^2_{reference}}$$

■ ASSOCIATED CONTENT

Supporting Information

Characterizations, NMR fluorescence spectra, X-ray data, and other supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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