

Electronic Supplementary Information

Copper Nanoparticles Generated by Aggregates of Hexarylbenzene derivative: A Reusable Catalyst for 'Click' Reaction

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General experimental methods

All the fluorescence spectra were recorded on SHIMADZU 5301 PC spectrofluorometer. UV spectra were recorded on Shimadzu UV-2450 PC spectrophotometer with a quartz cuvette (path length: 1 cm). The cell holder was thermostated at 25°C. Elemental analysis was done using a Flash EA 1112 CHNS/O analyzer of Thermo Electron Corporation. The dynamic light scattering (DLS) data were recorded with a Malvern Instruments Nano-ZS. The time-resolved fluorescence spectra were recorded with a HORIBA time-resolved fluorescence spectrometer. ¹H and ¹³C NMR spectra were recorded on a JEOL-FT NMR-AL 300 MHz spectrophotometer, Bruker (Avance II) FT-NMR-AL 400 and 500 MHz spectrophotometer using CDCl₃ as solvent and tetramethylsilane (Si(CH₃)₄) for internal standards. Data are reported as follows: chemical shifts in parts per million (d), multiplicity (s = singlet, br = broad signal, d = doublet, m = multiplet), coupling constants (Hz), integration, and interpretation. All spectrophotometric titration curves were fitted with SPECFIT 32 software. All spectral characterizations were carried out in HPLC-grade solvents at 20°C within a 10 mm quartz cell.

Fluorescence quantum yield: 9,10-Diphenylanthracene ($\Phi_f = 0.90$) in cyclohexane has been used as standard in the measurement of fluorescence quantum yield by using eqn (1), in which Φ_s is the radiative quantum yield of the sample; Φ_{fr} is the radiative quantum yield of the reference; A_s and A_r are the absorbance of the sample and the reference, respectively; D_s and D_r are the areas of emission for the sample and reference; L_s and L_r are the lengths of the absorption cells; and N_s and N_r are the refractive indices of the sample and reference solutions (pure solvents were assumed).

$$\Phi_{Fs} = \Phi_{Fr} \times \frac{1-10^{-A_r L_r}}{1-10^{-A_s L_s}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

Equation 1

Procedure for analytes sensing: UV-vis and fluorescence titrations were performed on 1 μ M solutions of ligand (3 μ l of CH₃CN are used to dissolve) in H₂O/ CH₃CN (5:5, v/v) with different metal ions such as Cu²⁺, Fe²⁺, Fe³⁺, Hg²⁺, Co²⁺, Pb²⁺, Zn²⁺, Ni²⁺, Cd²⁺, Ag⁺, Ba²⁺, Mg²⁺, K⁺, Na⁺, and Li⁺ as their chloride/perchlorate salts. In titration experiments, each time a 3 ml solution of **3** was filled in a quartz cuvette (path length, 1 cm) and spectra were recorded.

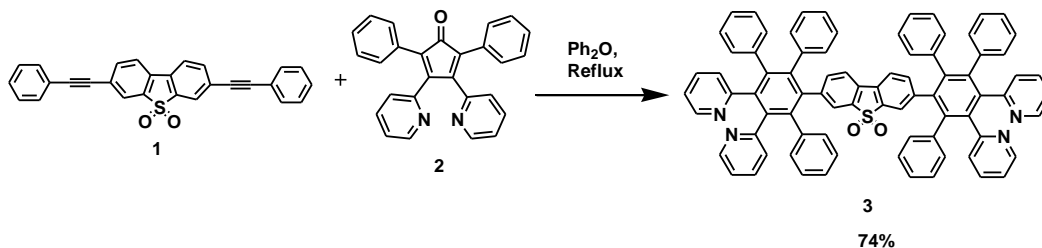
Fluorescence Lifetime (τ_f) Measurement. The time-resolved fluorescence spectra were recorded with a HORIBA time-resolved fluorescence spectrometer. Decays were monitored at the corresponding emission maximum of the compounds. In-built software allowed the fitting of the decay spectra ($\chi^2 = 1-1.5$) and yielded the fluorescence lifetimes. Decay curves were fitted either as a single exponential or multiexponential functions as:

$$F(t) = \sum F_i(0) \exp(-t/\tau_i)$$

where τ_i is the emission lifetime and $F_i(0)$ is the pre-exponential factor of the i^{th} component of the sample.

Experimental details

Synthesis of Compound (3). A solution of 3,7-bis(phenylethynyl)dibenzo[b,d]thiophene 5,5-dioxide **1**¹ (0.35 g, 1.0 mmol) and 2,5-diphenyl-3,4-di(pyridin-2-yl)cyclopenta-2,4-dienone **2**² (0.34 g, 1.05 mmol) in 2 mL of diphenylether was refluxed for 24 h under an inert atmosphere. Cold methanol (10 mL) was added to the reaction mixture. The methanol layer was decanted off, and the insoluble dark oil was subjected to column chromatography using 7:3 CHCl₃/hexane as the eluent. The compound was recrystallized from methanol to give **3** as a beige solid Yield 74%. ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, 4H, J = 4 Hz, ArH), 7.17-7.21 (m, 4H, ArH), 7.11 (s, 2H, ArH), 7.05 (d, 2H, J = 4 Hz, ArH), 6.94-6.96 (m, 10H, ArH), 6.83-6.92 (m, 25H, ArH), 6.73-6.76 (m, 6H, ArH), ¹³C NMR (125 MHz, CDCl₃): 115.01 (ArH), 115.74 (ArH), 119.13 (ArH), 120.94 (ArH), 121.27 (ArH), 121.36 (ArH), 121.88 (ArH), 121.96 (ArH), 122.13 (ArH), 122.26 (ArH), 122.81 (ArH), 123.65 (ArH), 126.17 (ArH), 126.27 (ArH), 126.54 (ArH), 126.69 (ArH), 129.84 (ArH), 131.60 (ArH), 132.14 (ArH), 134.07 (ArH), 134.66 (ArH), 135.15 (ArH), 134.59 (ArH), 135.94 (ArH), 136.53 (ArH), 137.90 (ArH), 143.01 (ArH), 153.90 (ArH), MS m/z 1133.35: [M + 1]⁺ calcd for C₈₀H₅₂N₄O₂S; C, 84.78%; H, 4.62%; N, 4.94%; S, 2.83%; found: C, 84.61%; H, 4.43%; N, 4.83%; S, 2.801.



Scheme S1. Synthesis of derivative **3**.

¹ Wang, C.; Dong, H.; Li, H.; Zhao, H.; Meng, Q.; Hu, W. *Crystal Growth & Design* **2010**, *9*, 10.

² Li, Z.; Zhang, L.; Wang, L.; Guo, Y.; Cai, L.; Yu, M.; Wei, L. *Chem. Commun.* **2011**, *47*, 5798.

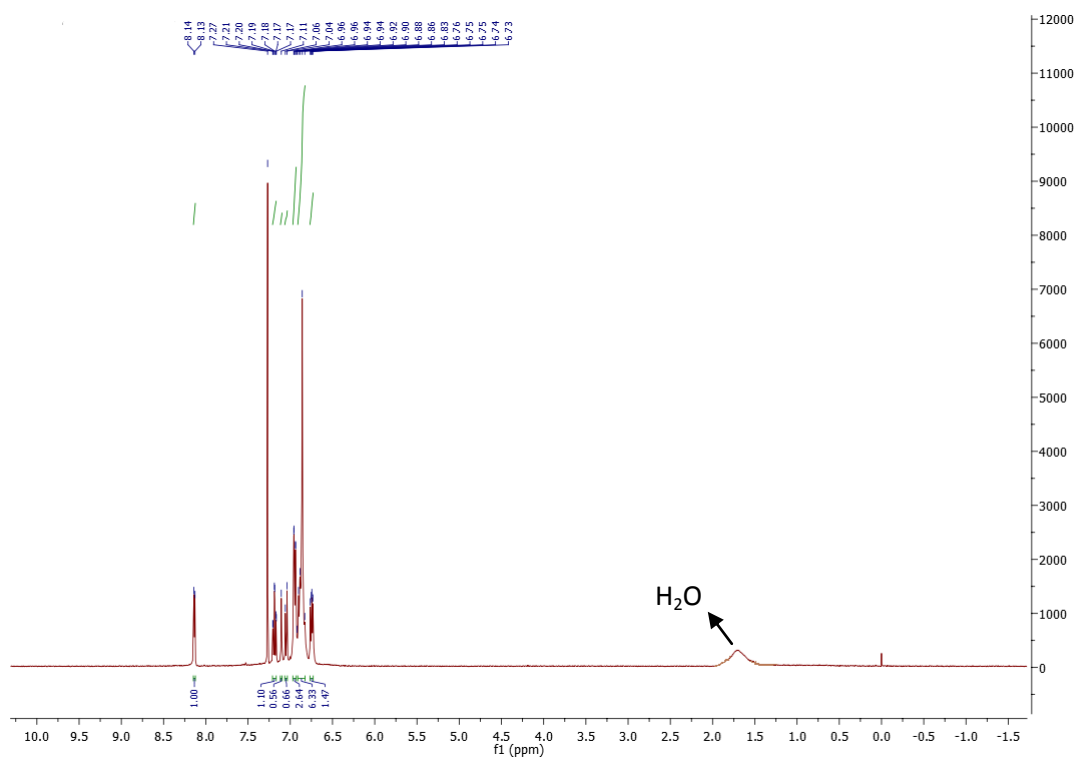


Fig. S1 ^1H NMR Spectra (CDCl_3 , 400 MHz, ppm) of compound 3.

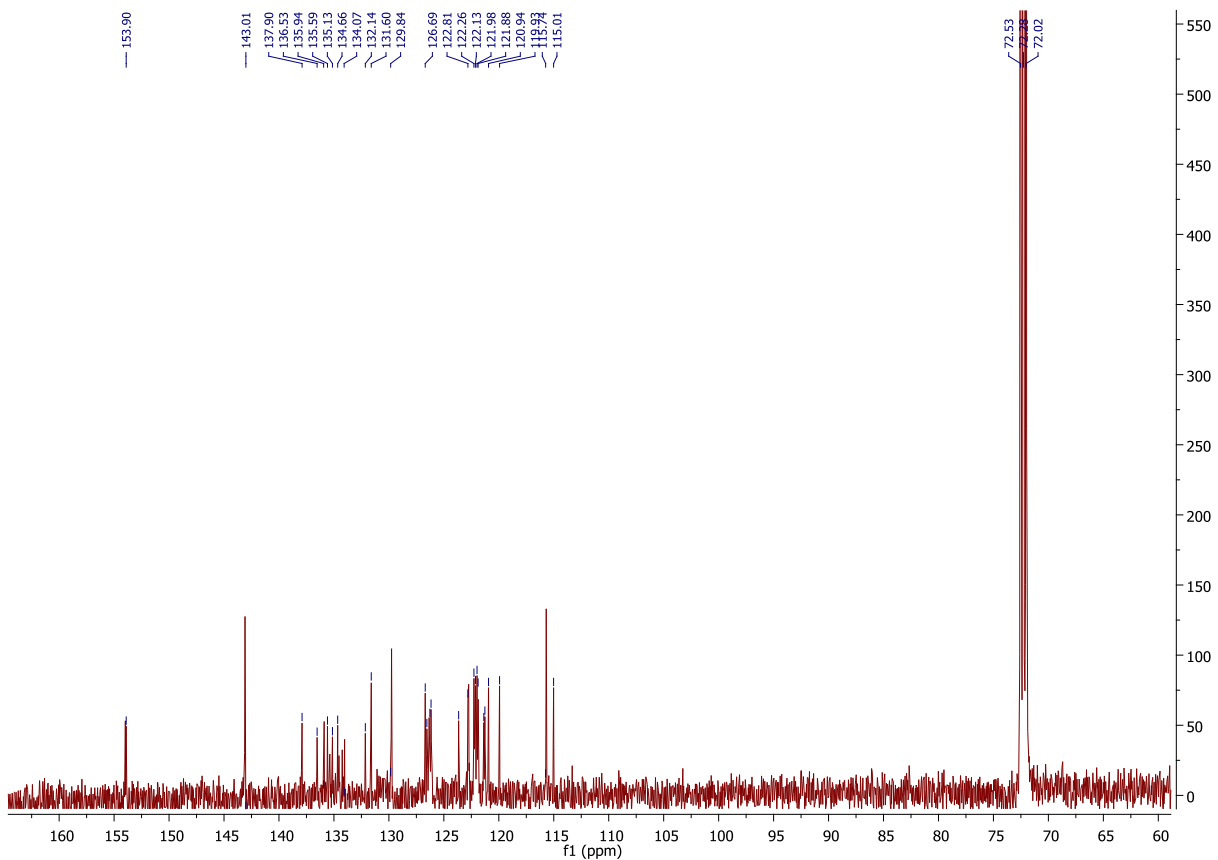


Fig. S2 ^{13}C NMR Spectra (CDCl_3 , 125 MHz, ppm) of compound 3:

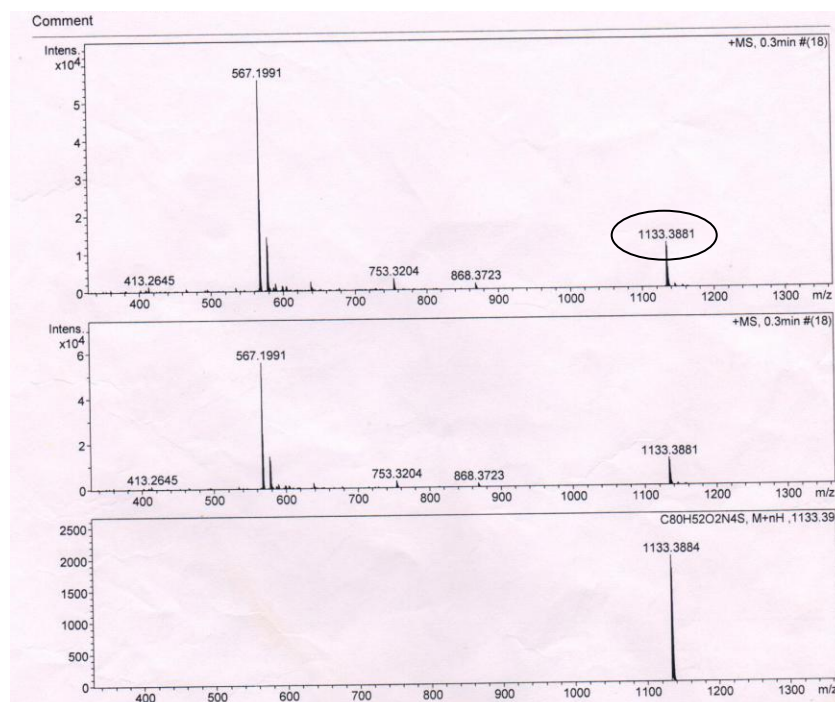


Fig. S3 Mass Spectrum (ESI-MS) of compound 3.

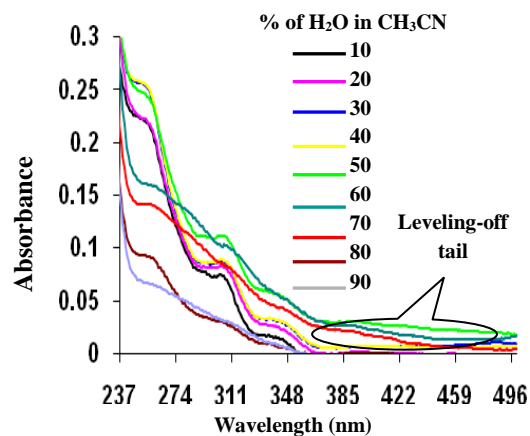


Fig. S4 UV-vis spectra of derivative **3** (1 μM) showing the variation of absorbance in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ mixture (0–90% volume fraction of water in CH_3CN).

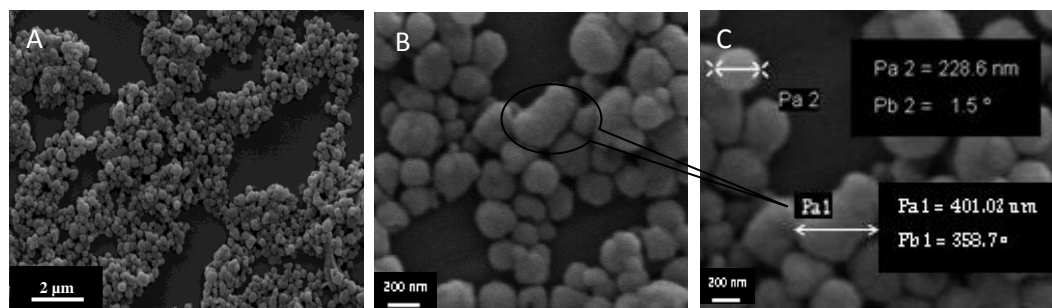


Fig. S5 Scanning electronic microscopy (SEM) images of derivative **3** in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (5/5) mixture.

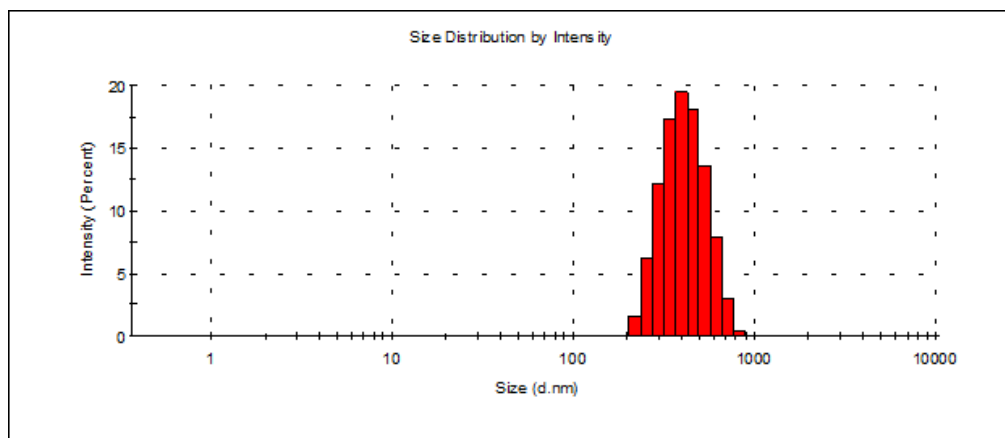


Fig. S6 The dynamic light scattering (DLS) studies derivative **3** showing the average diameter of aggregates is in the range of 400 nm in H₂O/CH₃CN (5/5).

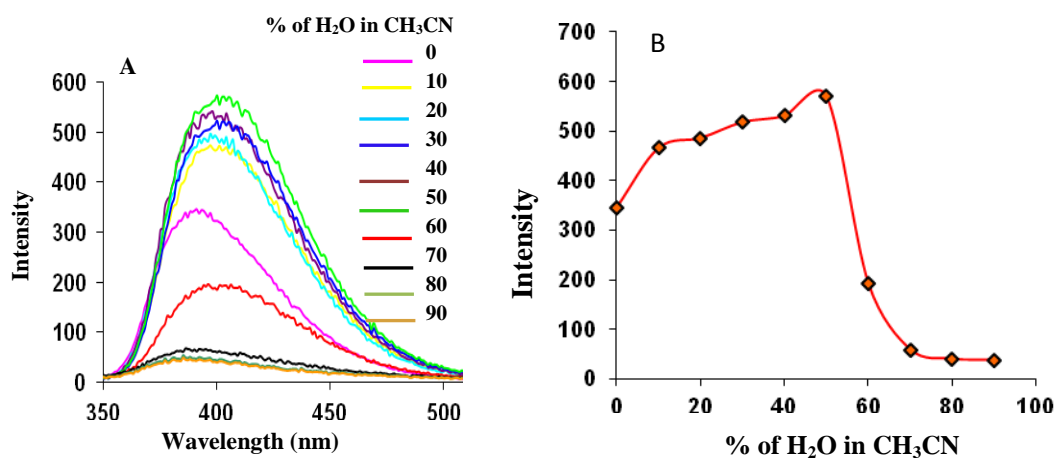


Fig. S7 (A) Fluorescence emission spectra of derivatives **3** (1 μM) in different ratios of H₂O/CH₃CN at λ_{ex} = 300 nm. (B) Change in fluorescence intensity with change in volume fraction of water in CH₃CN.

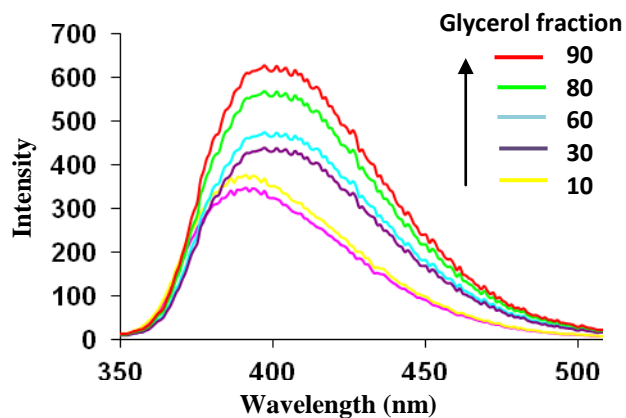


Fig. S8 Fluorescence spectra of derivative **3** (1 μM) showing the variation of fluorescence intensity in CH₃CN/glycerol mixtures with different glycerol fractions

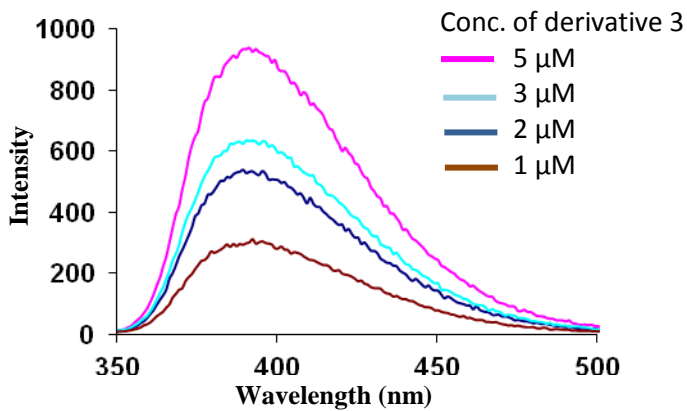


Fig. S9 The change in fluorescence spectra of derivative **3** in CH₃CN with increase in concentration.

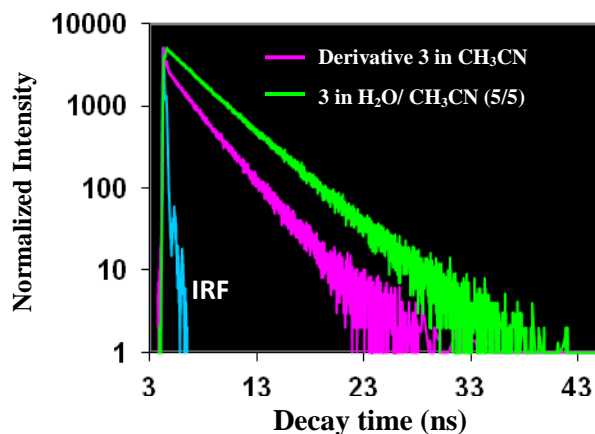


Fig. S10 Fluorescence lifetime decay profile of derivative **3** in pure CH₃CN (pink) and H₂O:CH₃CN (5/5) (green).

S. No	$\lambda_{\text{max}}^{\text{a}}$	Quantum yield ($\Phi_{\text{F}}^{\text{b}}$)	A_1/A_2^{c}	$\tau_{\text{F1}}^{\text{d}}$ (ns)	$\tau_{\text{F2}}^{\text{d}}$ (ns)	$\tau_{\text{av}}^{\text{e}}$ (ns)	k_{f}^{f} (10^9 S^{-1})	k_{nr}^{g} (10^9 S^{-1})
Derivative 3 in pure CH ₃ CN	390 nm	0.11	89.91/10.09	0.32	2.7	0.56	0.19	1.58
Derivative 3 in H ₂ O/CH ₃ CN (5/5)	405 nm	0.47	27.45/72.55	0.62	3.01	2.35	0.20	0.22

Table S1 Comparative photophysical properties of derivative **3** in CH₃CN and H₂O/CH₃CN (5/5): ^a emission maximum (nm). ^b Measured using a Quantaaurus-QY. ^c A_1 , A_2 : fractional amount of molecules in each environment. ^d τ_{F1} and τ_{F2} : biexponential life time of derivative **3** in CH₃CN and H₂O/CH₃CN (5/5). ^e τ_{av} :average life time decay. ^f radiative rate constant ($k_{\text{f}} = \Phi_{\text{F}}/\tau_{\text{av}}$). ^g nonradiative rate constant ($k_{\text{nr}} = (1 - \Phi_{\text{F}})/\tau_{\text{av}}$).

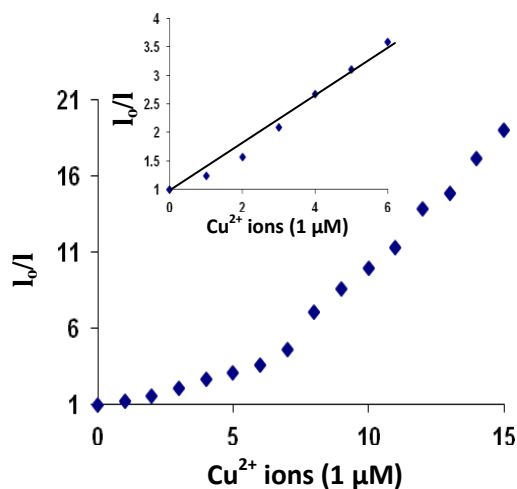


Fig. S11 Variation of fluorescence of aggregates of derivative **3** (1 μM) at 405 nm in H₂O/CH₃CN (1:1, v/v) buffered with HEPES, pH =7.0, λ_{ex} =300 nm in the presence of different concentrations of Cu²⁺ ions (I_0/I ; I_0 =initial fluorescence intensity at 405 nm; I = fluorescence intensity after the addition of Cu²⁺ ions at 405 nm).

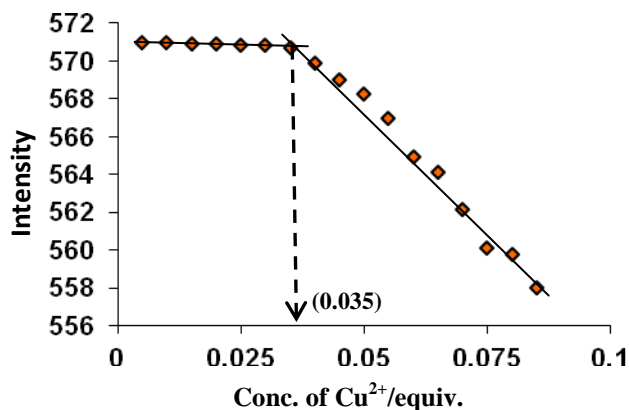


Fig. S12a: Showing the fluorescence intensity of derivative **3** at 405 nm as a function of Cu^{2+} ions concentration (equiv.) in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (5:5, v/v) buffered with HEPES, pH = 7.05, λ_{ex} = 300 nm.

To determine the detection limit, fluorescence titration of compound **3** with Cu^{2+} ions was carried out by adding aliquots of copper solution (in equiv.) and the fluorescence intensity as a function of Cu^{2+} ions added was then plotted. From this graph the concentration at which there was a sharp change in the fluorescence intensity multiplied with the concentration of receptor **3** gave the detection limit.

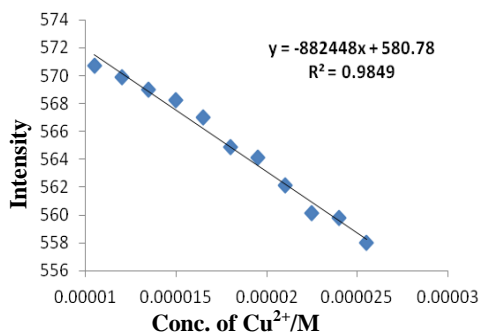
Equation used for calculating detection limit (DL):

$$\text{DL} = \text{CL} \times \text{CT}$$

CL = Conc. of Ligand; CT = Conc. of Titrant at which change observed.

Detection limit (DL) of Cu^{2+} ions with **3:**

$$\text{Thus; DL} = 0.035 \times 10^{-6} = 35 \times 10^{-9} = 35 \text{ nM.}$$



Multiple R = 0.99242

$R^2 = 0.9849$

Standard deviation = 0.009,

Observation = 11,

Intercept = 580.78

Slope = 882448

Figure S12b: Calibrated curve showing the fluorescence intensity of compound **3** at 405 nm as a function of Cu^{2+} ions concentration (equiv.) in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (5:5, v/v) buffered with HEPES, pH = 7.05, λ_{ex} = 300.

For comparison we have calculated the detection limit by another method (reference: *Dalton Trans.* **2013**, *42*, 15113–15119)

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of receptor **3** without Cu^{2+} was measured by 11 times and the standard deviation of blank measurements was determined. The detection limit is then calculated with the following equation:

$$\text{DL} = 3 \times \text{SD}/\text{S}$$

Where SD is the standard deviation of the blank solution measured by 10 times; S is the slope of the calibration curve.

From the graph we get slope

S = 882448, and SD value is 0.009

Thus using the formula we get the Detection Limit

$$(\text{DL}) = 3 \times 0.009/882448 = 30.5 \times 10^{-9} \text{ M} = 30.5 \text{ nM}$$

i.e. probe **3** can detect Cu^{2+} ions in this minimum concentration through fluorescence method.

Reference: Goswami, S.; Das, S.; Aich, K.; Sarkar, D.; Kumar, T. M.; Quah, C. K.; Fun, H. K. CHEF induced highly selective and sensitive turn-on fluorogenic and colorimetric sensor for Fe^{3+} . *Dalton Trans.* **2013**, *42*, 15113–15119.

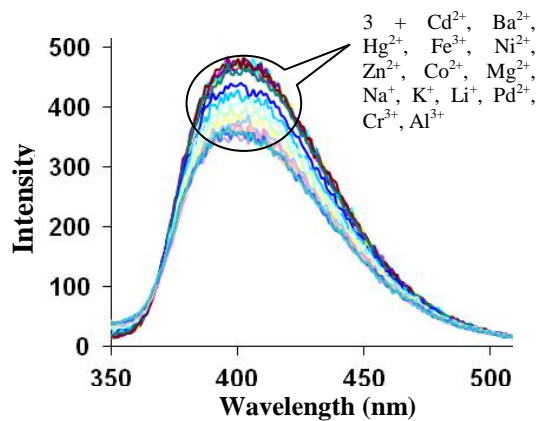


Fig. S13 Change in the fluorescence spectra of compound **3** (1 μ M) upon additions of metal perchlorates/chloride (50 μ M) in CH₃CN/water (1:1) buffered with HEPES, pH = 7.05.

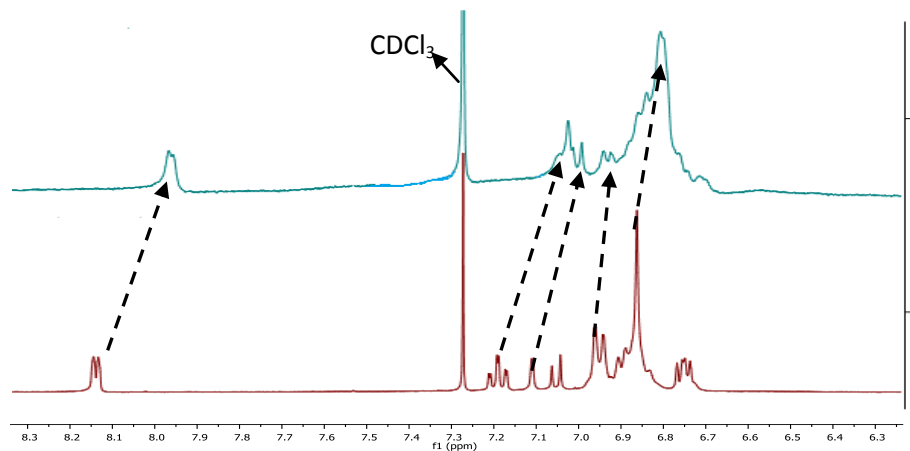


Fig. S14 Overlay ¹H NMR spectra of derivative **3** (red) and copper nanoparticle (blue) respectively, after filtration with THF and CHCl₃.

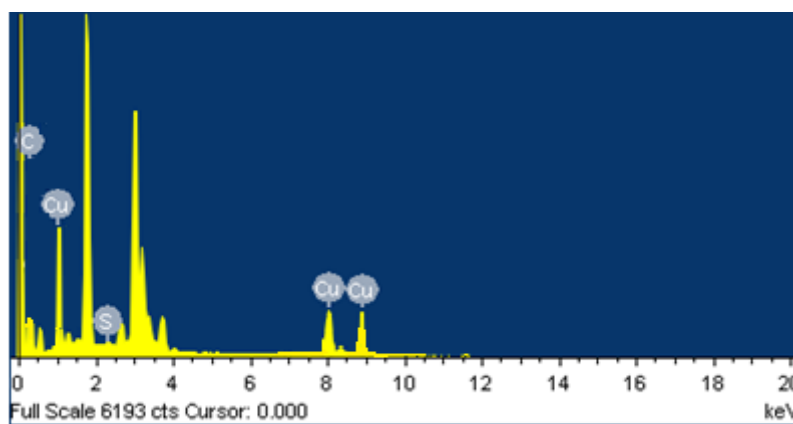


Fig. S15 The SEM-EDX spectrum of aggregates of **3** in presence of copper chloride show the presence of copper nanoparticles.

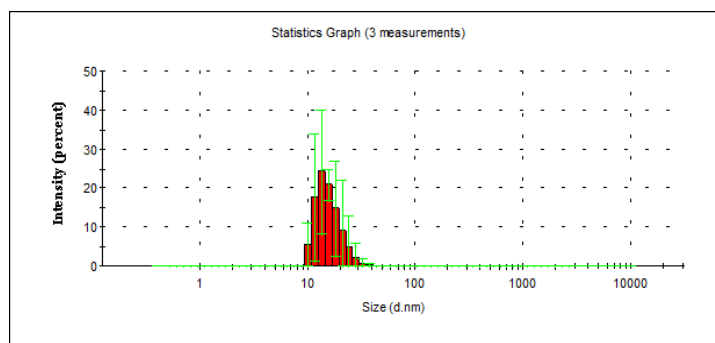


Fig. S16 The dynamic light scattering (DLS) studies of derivative **3** in presence of 20 equiv. of CuCl_2 ions, showing the average diameter of copper nanoaggregates is 13.54 nm.

CuAAC (procedure and ^1H NMR of final products):

Synthesis of copper Nanoparticles. To a 3 ml solution of derivative **3** (0.1 mM) was added 60 μl of 10^{-1} M solution of CuCl_2 (20 equiv.) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v). The reaction was stirred at room temperature for 10 min and formation of nanoparticles take place. These nanoparticles solution was used as such in the catalytic experiment.

General procedure for the CuNPs catalyzed azide-alkyne 'click' reaction: A 25 ml round bottom flask is charged with solution with 1.05 mmol of alkyne and 1 mmol of organic azide and 0.1% mol of nano catalyst (CuNPs). The reaction mixture is stirred during 25 to 30 min at room temperature under N_2 . The final product is extracted from water with CH_2Cl_2 (3 x 5 mL). The organic layer is dried with Na_2SO_4 and the solvent is removed *in vacuo* to give the corresponding 1,2,3-triazole. The product is then purified by silica chromatography.

A typical procedure for the catalyst-reusing sequence in the CuNPs-catalyzed 'Click' reaction: After the reaction was performed under the conditions of Table 1, 1.05 mmol of alkyne and 1 mmol of organic azide were added to the reaction mixture. It was used next catalytic sequence under the same reaction conditions as first cycle. In each cycle the reactants are fully consumed within 25 to 35 min. It was observed that after five recycles, the isolated yield of corresponding product was still up to 90%, which indicates that nano catalyst CuNPs have high catalytic activity and stability in our experimental conditions (Table 1). Thus, the CuNPs can be recycled and at least five times without significant loss of their catalytic activity.

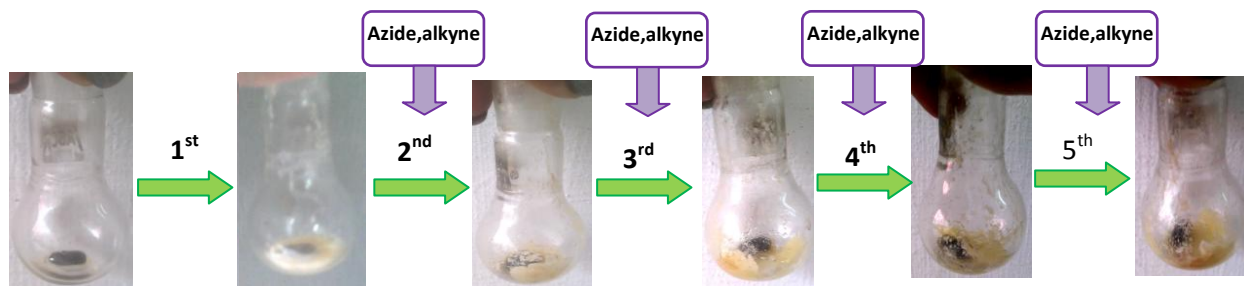
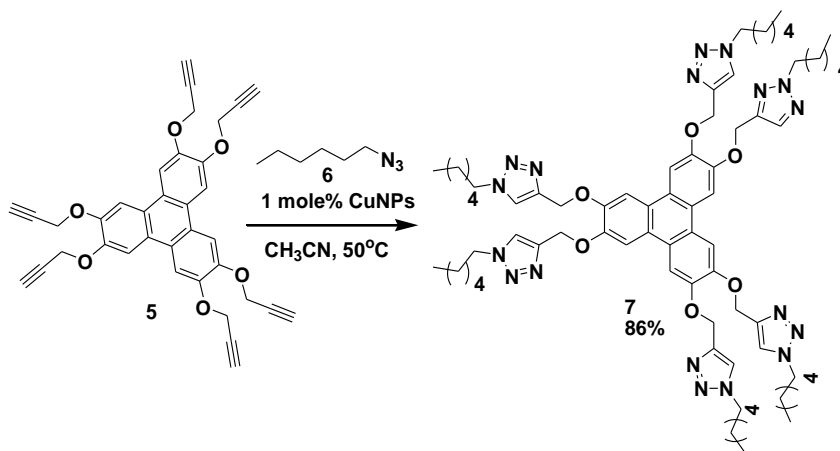


Figure S17. Depiction of the catalyst-reusing for entry 4 in Table 1.

CuNPs catalyzed cycladdition reaction between hexyl Azide and Phenyl Acetylene Using Various Amounts of CuNPs: A 25 ml round bottom flask is charged with solution with 1.05 mmol of phenyl acetylene and 1 mmol of hexyl azide and (1-0.0005 mol %) of nano catalyst (CuNPs). The reaction mixture is stirred during 25 min to 15 h at room temperature under N₂. The final product is extracted from water with CH₂Cl₂ (3 x 5 mL). The organic layer is dried with Na₂SO₄ and the solvent is removed *in vacuo* to give the corresponding 1,2,3-triazole. The product is then purified by silica chromatography.

Synthesis of Compound (7). A 25 ml round bottom flask is charged with solution with 1.05 mmol of 2,3,6,7,10,11-hexakis(prop-2-ynoxy)triphenylene **5** and 1 mmol of hexyl azide **6** and 0.1% mol of nano catalyst (CuNPs) in 2 ml of CH₃CN. The reaction mixture is stirred during 15 h at 50°C. The final product is extracted from water with CH₂Cl₂ (3 x 5 mL). The organic layer is dried with Na₂SO₄ and the solvent is removed *in vacuo* to give the corresponding 1,2,3-triazole. The product is then purified by silica chromatography.



Scheme S2. Synthesis of Triphenylene-based discotic liquid crystal **7** bearing 1,2,3-triazole groups using “click” chemistry in presence of 1 mole% CuNPs

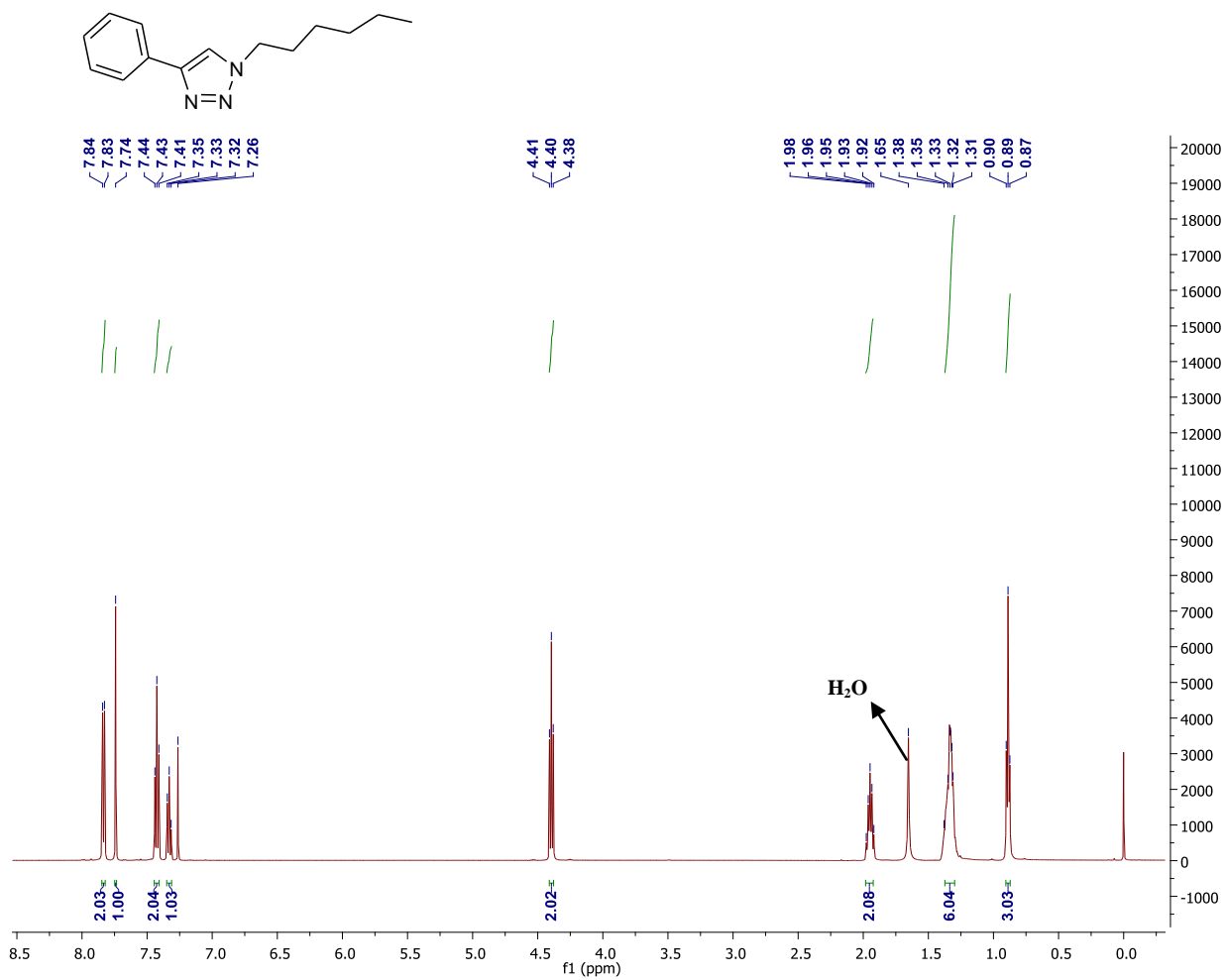


Fig. S18 ^1H NMR spectrum of **1-hexyl-4-phenyl-1H-1,2,3-triazole** (CDCl_3 , 500 MHz, ppm)

^1H NMR (500 MHz, CDCl_3) δ ppm: 7.84 (d, 2H), 7.74 (s, 1H), 7.41-7.44 (m, 2H), 7.32-7.35 (m, 1H), 4.39 (t, 2H), 1.92-1.98 (m, 2H), 1.31-1.38 (m, 6H), 0.89 (t, 3H).

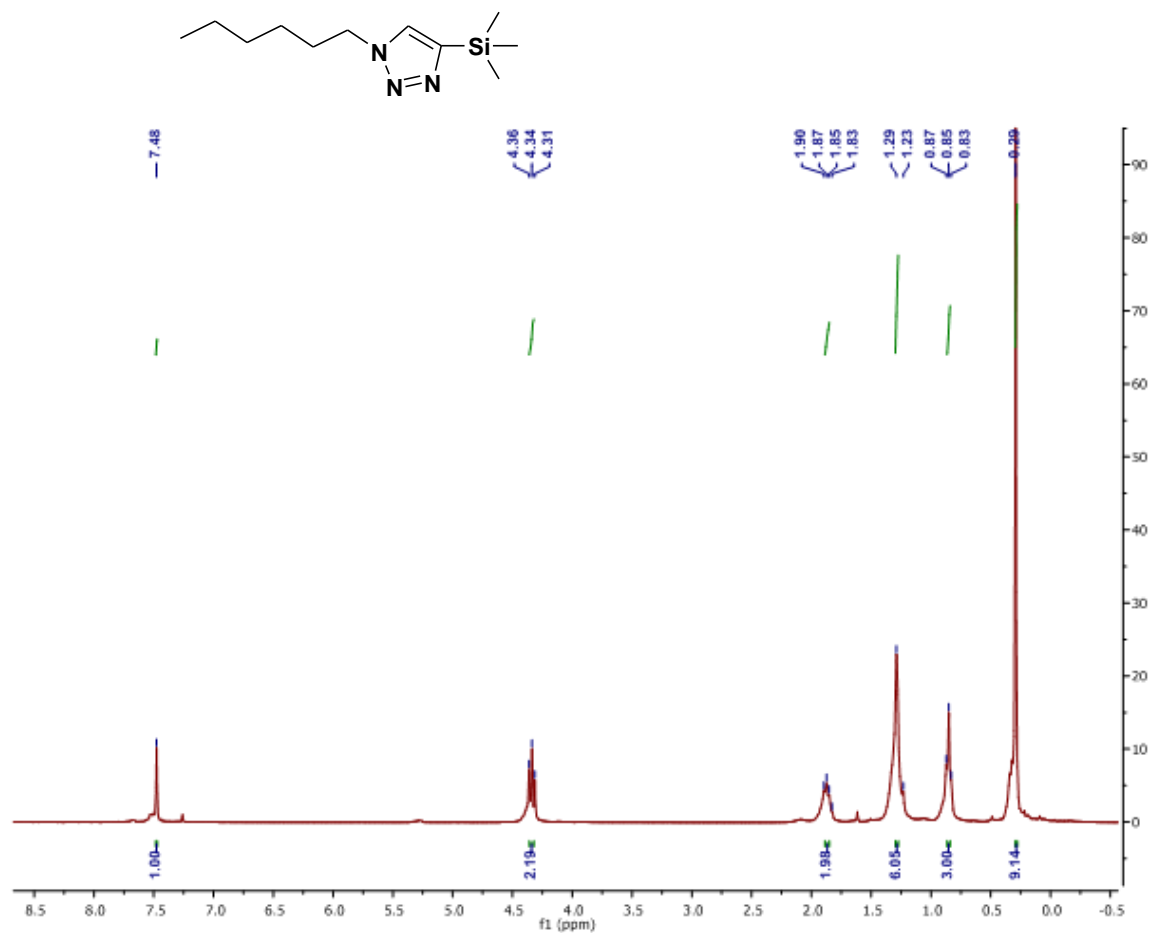


Fig. S19 ¹H NMR spectrum of **1-hexyl-4-(trimethylsilyl)-1H-1,2,3-triazole** (CDCl₃, 300 MHz, ppm)

¹H NMR (500 MHz, CDCl₃) δ ppm: 7.48 (s, 1H), 4.33 (t, 2H), 1.83-1.90 (m, 2H), 1.23-1.29 (m, 6H), 0.85 (t, 3H), 0.29 (s, 9H)

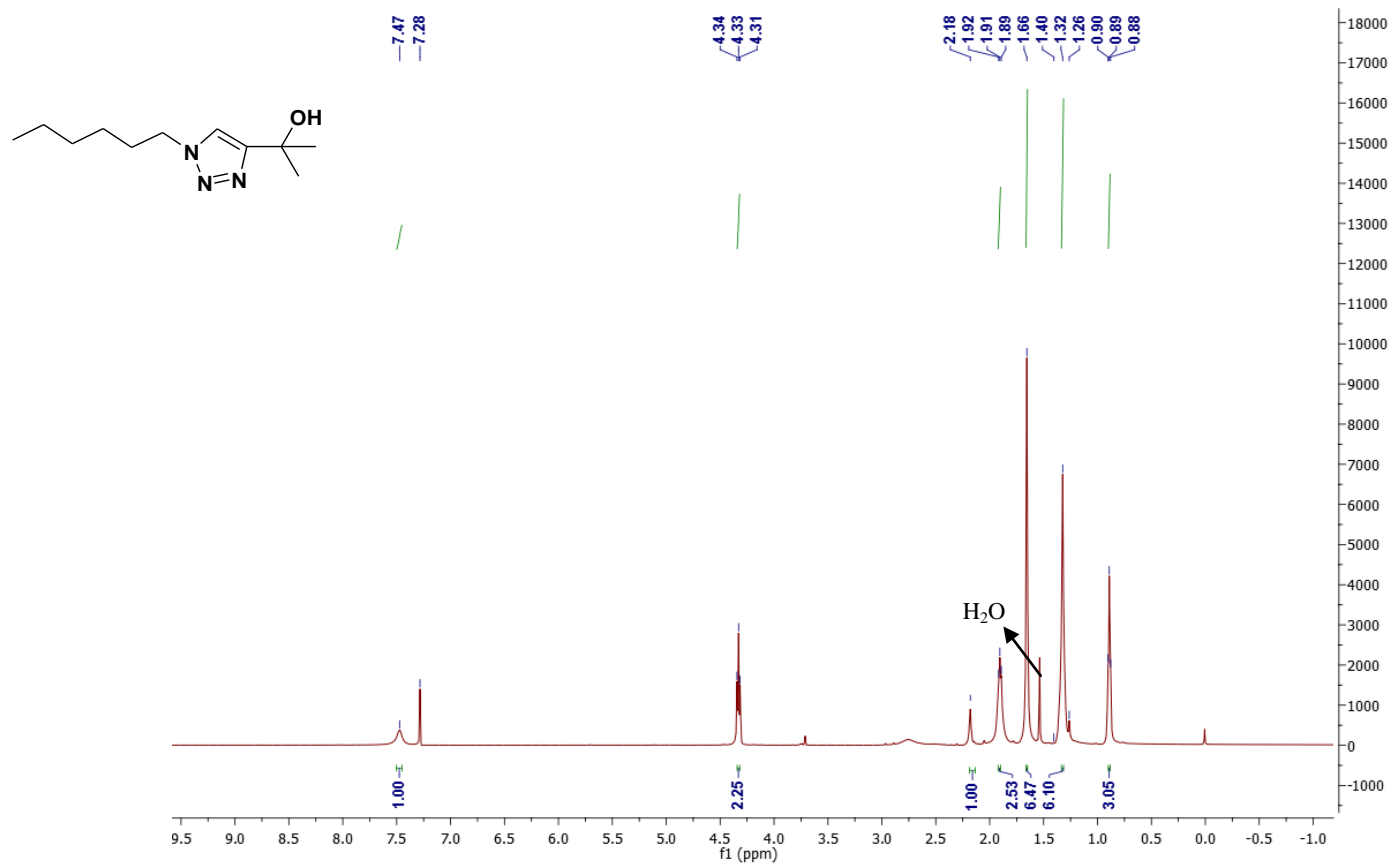


Fig. S20 ^1H NMR spectrum of **2-(1-benzyl-1H-1,2,3-triazol-4-yl)propan-2-ol** (CDCl_3 , 500 MHz, ppm)

^1H NMR (500 MHz, CDCl_3) δ ppm: 7.47 (s, 1H), 4.33 (t, 2H), 2.18 (s, 1H), 1.89-1.92 (m, 2H), 1.66 (s, 6H), 1.26-1.40 (m, 6H), 0.89 (t, 3H)

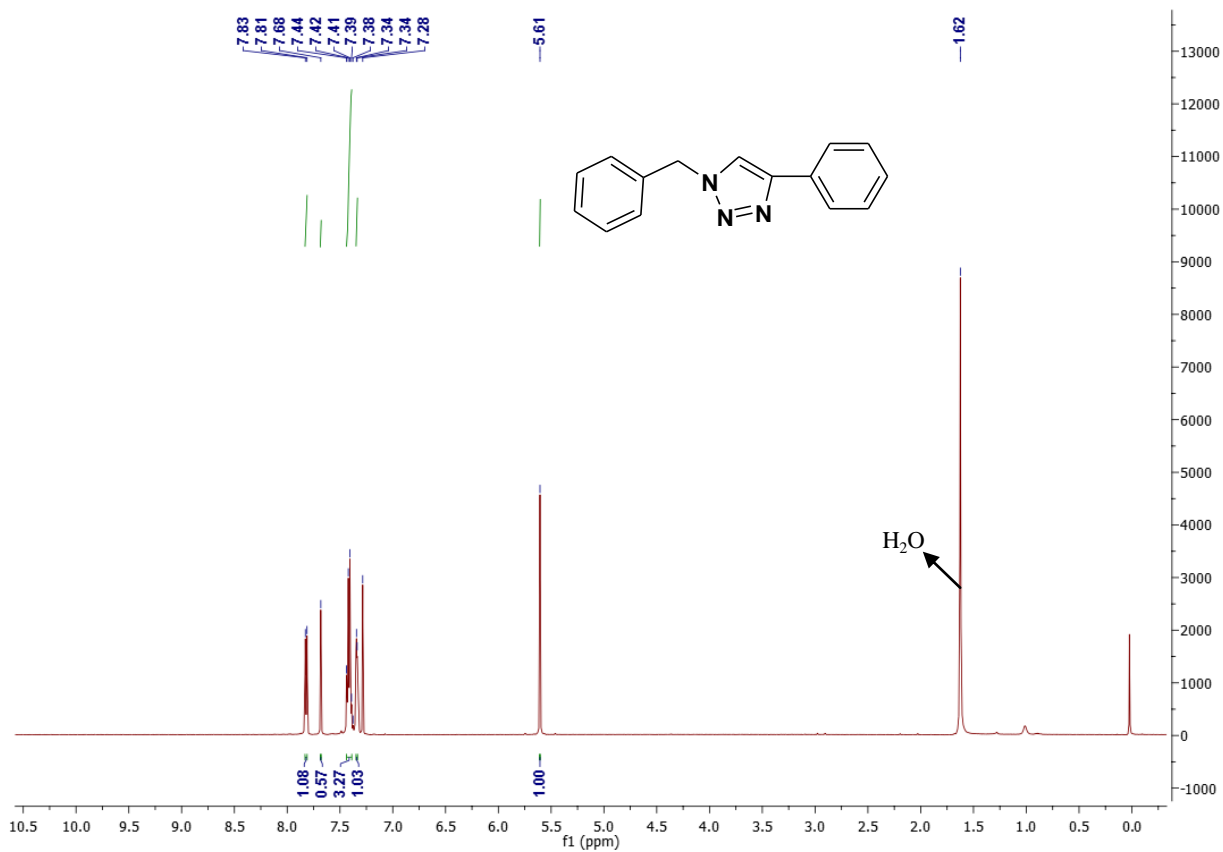


Fig. S21 ^1H NMR spectrum of **1-benzyl-4-phenyl-1H-1,2,3-triazole** (CDCl_3 , 500 MHz, ppm)

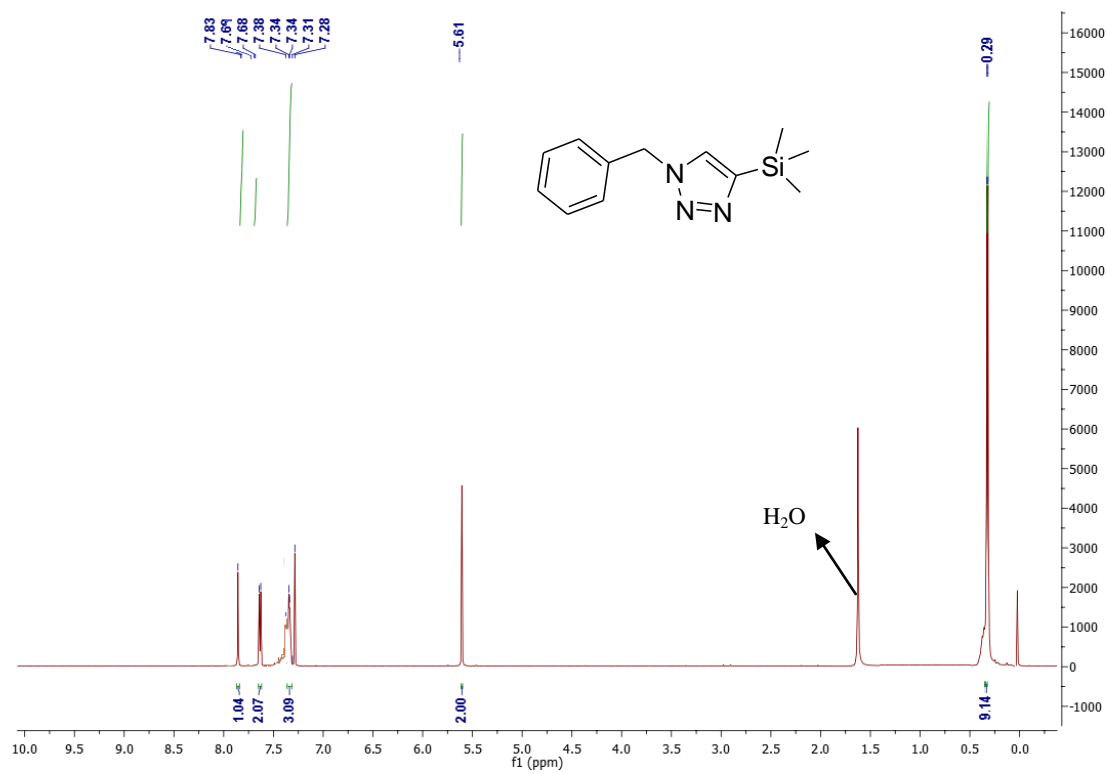


Fig. S22 ^1H NMR spectrum of **1-benzyl-4-(trimethylsilyl)-1H-1,2,3-triazole** (CDCl_3 , 500 MHz, ppm)

^1H NMR (500 MHz, CDCl_3) δ ppm: 7.83 (s, 1H), 7.69 (d, 2H), 7.28-7.38 (m, 3H), 5.61 (s, 2H), 0.29 (s, 9H).

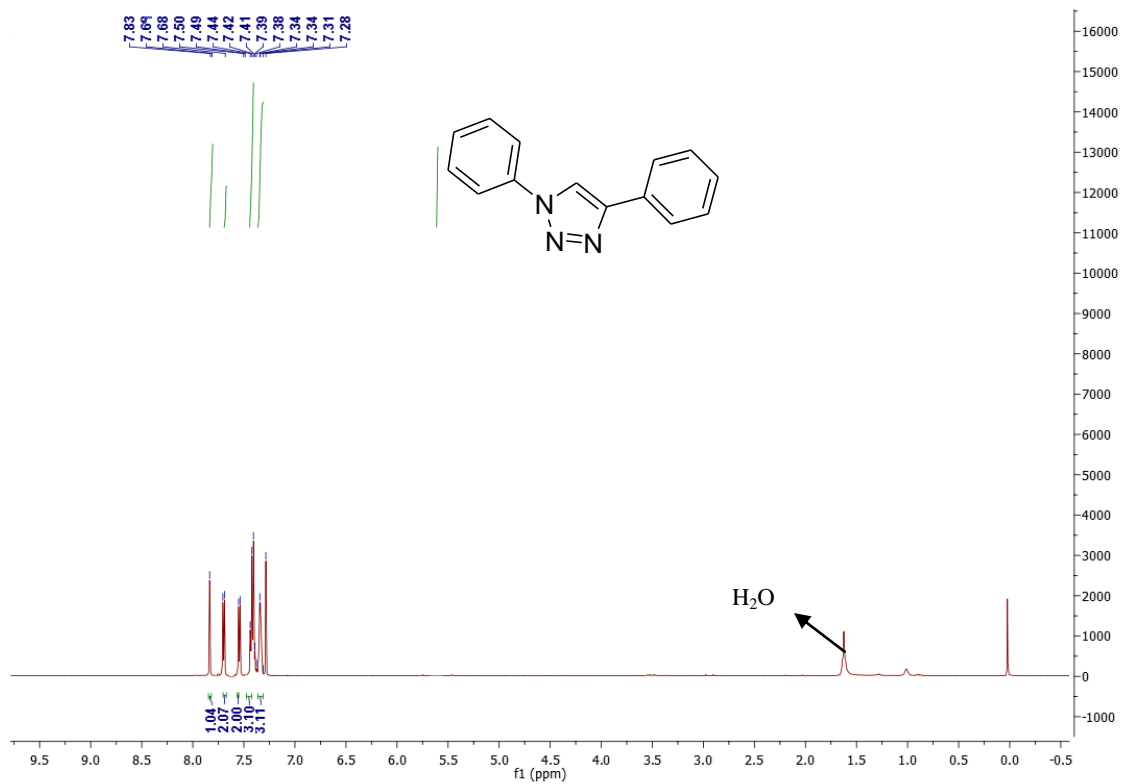


Fig. S23 ¹H NMR spectrum of **1,4-diphenyl-1H-1,2,3-triazole** (CDCl₃, 500 MHz, ppm)

¹H NMR (500 MHz, CDCl₃) δ ppm: 7.83 (s, 1H), 7.69 (d, 2H), 7.50 (d, 2H), 7.38-7.49 (m, 3H), 7.28-7.38 (m, 3H).

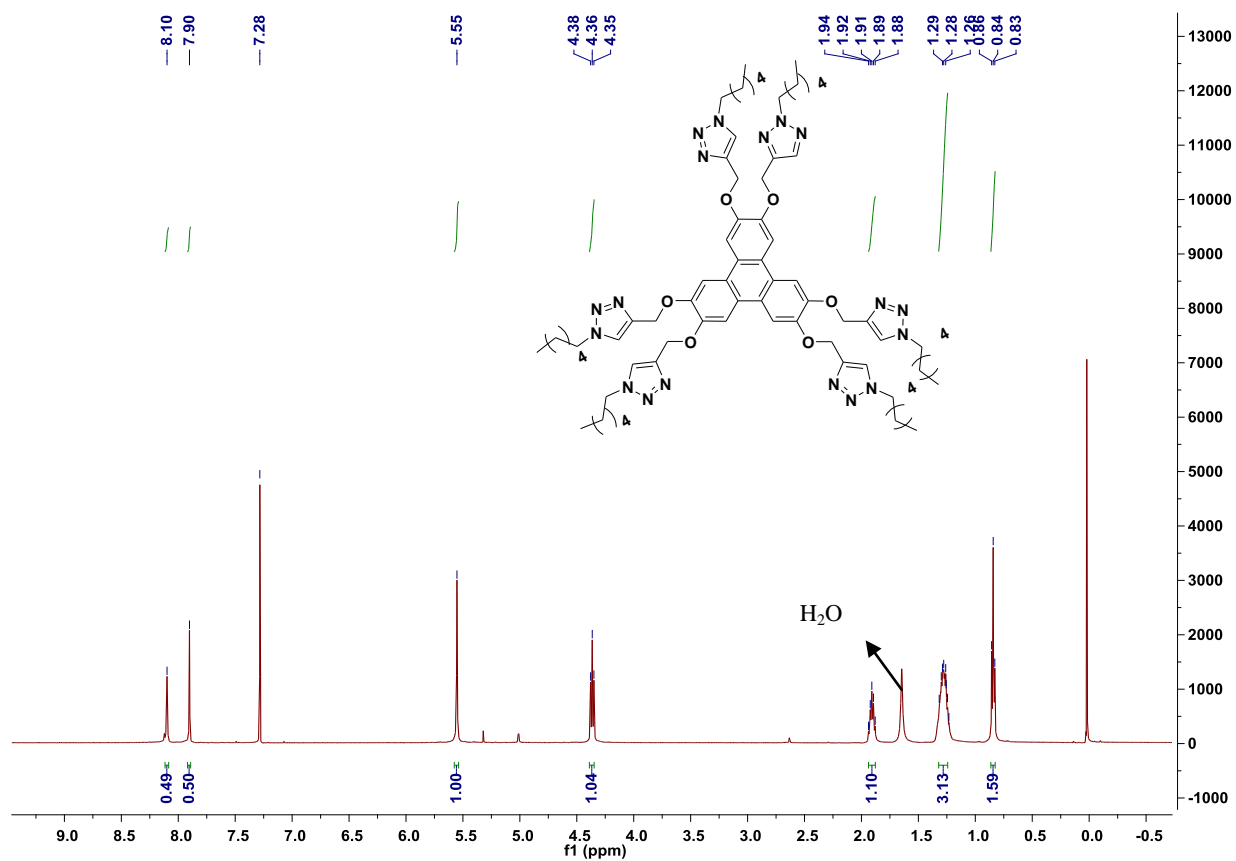


Fig. S24 ^1H NMR spectrum of derivative **7** (CDCl_3 , 500 MHz, ppm)

^1H NMR (500 MHz, CDCl_3) δ ppm: 8.10 (s, 6H), 7.90 (s, 6H), 5.55 (s, 12H), 4.36 (t, 12H), 1.88-1.94 (m, 12H), 1.26-1.29 (m, 36H), 0.84 (t, 18H).

Table S2: Comparison of present method over other reported procedure in literature for the preparation of copper nanoparticles.

Entry	Method of formation of copper nanoparticles	Size of copper nanoparticles	Reaction time to prepare copper nanoparticles	Reducing agent or surfactants	Reaction temp. (°C)	Nanoparticles	Journals
1.	Wet chemical method	13 nm (average)	15 min	no	Room temp.	Copper Nanoparticles (Cu NPs)	Present manuscript
2.	Chemical method	8-10 nm	3 hrs	Hydrazine hydrate	40 °c	Cu NPs	ACS Appl. Mater. Interfaces 2013, 5, 3839
3.	Biosynthesis	15-20 nm	24 hrs	-----	35 °C	Cu NPs	Nanoscale, 2013, 5, 2300
4.	chemisorption–hydrolysis method	4.7 nm	Over night	NH ₄ OH	350 °C	Cu NPs	ACS Catal. 2014, 4, 2818
5.	Chemical method	8-27 nm	10 hrs	NaOH	130 °C	CuO	RSC Adv., 2012, 2, 1387
6.	Chemical method	2 nm	8 hrs	140 °C	Cu NPs	<i>Chem. Commun.</i> , 2012, 48, 3784
7.	Chemical method	-----	10-15 min	NaOH	60 °C	Cu ₂ O	CrystEngComm, 2012, 14, 8454
8.	Thermal decomposition	60 nm	4 hrs	-----	350 °C	CuO	CrystEngComm, 2013, 15, 4077
9.	Synthesis of copper nanoparticles using ionic liquids	10 nm	5 hrs	Utilizing ionic liquids	-----	Cu NPs	Ind. Eng. Chem. Res. 2013, 52, 794
10.	Thermal decomposition of polymer	50-70 nm	-----	450°C	CuO	<i>New J. Chem.</i> , 2014, 38, 4267
11.	Thermal reduction	28 nm	1 hr	triphenylphosphine	140°C	Cu NPs	doi.org/10.1016/j.bioorg.2014.07.004
12.	Chemical reduction	98 nm	3 hrs	NaH ₂ PO ₂ ·H ₂ O	140°C	Cu NPs	Eur. J. Inorg. Chem. 2013, 4940
13.	Polymer based micellar method	36.6 nm	30 min	NaBH ₄	-----	Cu NPs	RSC Adv., 2014, 4, 14193

Table S3: Comparison of catalytic efficiency of generated CuNPs for CuAAC (Cu catalyzed azide-alkyne ‘click’ reaction) in present manuscript with literature Reports.

Entry	reference	Catalyst	Conc. of catalyst	solvent	Time	Temp.
1.	Present manuscript	Copper nanoparticles	1 mole%	neat	0.41 H	RT
2.	<i>J. Am. Chem. Soc.</i> 2012, 134 , 9285.	poly(imidazole-acrylamide)/CuSO ₄ /NaAsc	0.25 mol%	t-BuOH/ H ₂ O 1/3	1.5 h	50 °C
3.	<i>Green Chem.</i> , 2012, 14 , 1298.	Cu-nanoparticulates in Guar-gum	10 W%	EtOH	5 h	RT
4.	<i>J. Org. Lett.</i> 2008, 10 , 497.	Cu/AlO(OH)	3 mol%	n-hexane	6 H	25 °C
5.	<i>Green Chem.</i> 2011, 13 , 3440.	ammonium NHC-CuI	5 mol%	H ₂ O	3 H	20 °C
6.	<i>J. Tetrahedron Letters</i> 2014, 55 , 2312	Nano-copper	5 mol%	EtOH	8 H	RT
7.	<i>Green Chem.</i> 2012, 14 , 625–632.	nano-FGT-Cu	2.4 mol%	HO	0.16 H	Mw 120
8.	<i>Chem. Commun.</i> , 2008, 741	[Cu(C18 ₆ tren)]Br	0.005 mol%	toulene	24 H	60 °C
9.	<i>Appl. Catal., A</i> 2013, 453 , 151–158.	CuSO ₄ /N ₂ H ₄ -H ₂ O	0.0025 mol%	H ₂ O	4 H	20 °C
10.	<i>Chem. Commun.</i> , 2013, 49 , 11358.	Cu(I)-NHC	1 mol%	H ₂ O	18 H	RT
11.	<i>Green Chem.</i> , 2012, 14 , 622.	Cu@FeNPs	5 mol%	H ₂ O	12 H	RT
12.	<i>Org. Biomol. Chem.</i> , 2011, 9 , 6385	CuNPs on activated carbon	5 mol%	H ₂ O	7 H	70 °C