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One-Pot Synthesis of Hydrazono-Sulfonamide Adducts using Cu(BTC) MOF Catalyst and Their Remarkable AIEE Properties: Unprecedented Copper(II)-Catalyzed Generation of Ketenimine

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Abstract: An efficient, four-component reaction for the synthesis of hydrazono-sulfonamide adducts *via* in situ generated ketenimine was discovered. Highly porous copper benzenetricarboxylate [Cu(BTC)], metal-organic frameworks (MOF) was used as a heterogeneous catalyst for four-component coupling reaction involving aldehyde, alkyne, tosyl azide, and phenylhydrazine in one pot process. For the first time, copper(II) catalyst was utilized to generate ketenimine intermediate. The Cu(BTC) catalyst was recycled and reused for six times without any substantial loss in the yield. In addition, pyrene adduct (**5r**) shows remarkable aggregation induced emission enhancement (AIEE) property, which was studied in detail using THF: Water solvent mixtures. Adduct **5r** is almost non-emissive in pure THF solution, however, it emits greenish-yellow colour in the aggregated state. Formation of nano-aggregates was confirmed by TEM analysis. A theoretical DFT study supports the observed photophysical changes.

Introduction

Multi-component reactions[1] (MCRs) are consistently used as a powerful tool to build molecules with complex framework. Trapping of in situ generated reactive species to construct active motifs is the crux of MCRs mechanisms. Ketenimine[2] is one of such functionality and perfectly suitable for in situ generation and further sequential reaction with other substrates leading to the construction of special molecules *via* MCR technique. Wang et al[3], Chang et al[4] and others[5] developed efficient protocols for various active motifs bearing cyclic and acyclic structures by reacting in situ generated ketenimines with various substrates. Most of the literatures were reported to generate ketenimines using homogeneous Cu(I) catalyst and these reactions has some disadvantages such as metal contamination, difficult workup process, poor yield, and high cost of the catalyst. Very few ketenimine synthetic protocols make use of heterogeneous catalyst derived from Cu(I) source.[5d, f, q]

A metal organic framework[6] (MOF) is very important class of highly porous materials that are composed of metal ions-organic ligands polymeric linkages. Unique properties of MOF's such as high surface area, flexibility, pore size distribution makes them suitable to find potential applications in many fields such as drug delivery[7], gas storage and separation[8], sensors[9], etc. Owing to their excellent properties and catalytic nature, chemists have employed MOF as solid catalyst for many organic transformations in past several years.[10] These findings encouraged us to perform cascade reactions using Cu-MOF[11] as a heterogeneous catalyst to generate ketenimine and its application in novel MCR. In the present work, we report the reactant accelerated generation of ketenimine by reaction of alkyne and tosyl azide using heterogeneous Cu(BTC) catalyst and which was further react with aromatic hydrazone (generated in situ by reaction of aromatic aldehyde and phenylhydrazine) to afford hydrazono-sulfonamide adducts in one-pot operation (Figure 1). Following this excellent method, we synthesized a small library of structurally diverse hydrazono-sulfonamide adducts. An efficient and remarkable heterogeneous Cu(BTC) catalyst was recovered and reused in six times without affecting the catalytic activity and yield of adducts. To the best of our knowledge, this is the first report application of Cu(BTC)[11b, d-i] MOF for generation of ketenimine. In continuation, aggregation Induced emission enhancement (AIEE) property of pyrene adduct (**5r**) was studied in detail.

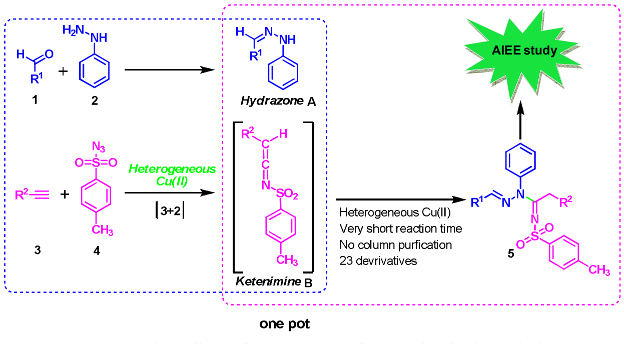


Figure 1. General outline of one-pot synthesis of substituted-(hydrazono-sulfonamide) adducts

Results and Discussion

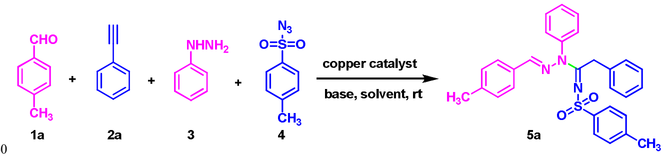
In this study 4-methylbenzaldehyde (**1a**), phenylhydrazine (**3**), phenylacetylene (**2a**) and tosyl azide (**4**) were used as model substrates. Various catalysts, bases and solvents were screened to get maximum yield. All reactions were performed under aerobic conditions. The product was not formed in the absence of catalyst. On the other hand, the reaction was performed using triethylamine (TEA) in the presence of CuI in dichloromethane (DCM) afforded 87% of desired product (Table 1, Entry 2). Structure of **5a** was characterized using ^{1}H NMR, ^{13}C NMR, and ESI-MS analysis. Single crystal XRD analysis unambiguously confirmed the structure of **5a** (see Supporting Information). Various Cu(I) and Cu(II) catalysts were screened using this protocol. All catalysts, except CuI, gave poor-to-moderate yields (10% to 67%) of desired adduct.

We preferred to use solid supported catalyst in order to develop a metal contamination free, environment-friendly methodology with simple workup. Very recently Konar et al[12] reported, Cu(II) MOF catalyzed Glaser type homo-coupling reactions. The mechanism outlined in the report suggested that electron rich ligands present in MOF facilitates in situ reduction of Cu(II) to Cu(I). Cu(I), the active species for homo-coupling reactions is oxidized into Cu(II) at the end of the reaction without affecting heterogeneous nature of the solid catalyst. Motivated by this finding, we envisaged that in situ generated hydrazones could reduce Cu(II) to Cu(I) species which can generate ketenimine intermediate. To ascertain our hypothesis, four component coupling reaction were performed using Cu(BTC) MOF as a heterogeneous catalyst under standard conditions. To our surprise, without affecting the heterogeneity nature of the catalyst, the reaction was progressed smoothly to furnish the desired product in excellent yield (Table 1, Entry 9). In fact, the yield of **5a** was higher than the reaction performed using homogeneous catalyst.

Encouraged by these results, we focused our efforts to optimize the quantity of catalyst needed to perform the coupling reaction. Maximum yield (1.9 g) was obtained when 2.5 mg (1 mol%) of the catalyst was used under standard reaction condition. Increase in the loading of catalyst did not result in higher yield. The reaction was carried out using lower amount of catalyst afforded low yield (Table 1, Entry 23 and 24). Over all, various inorganic and organic bases were screened, among them, TEA was found to be the best to afford **5a** in good yield. Various solvents were screened for the coupling reactions such as dichloroethane (DCE), tetrahydrofuran (THF), acetonitrile (ACN), chloroform, toluene, xylene, 1,4-dioxane, *N,N*-dimethylformamide (DMF), and DCM, among them DCM emerged as a most suitable solvent. The equimolar mixture of reactants, Cu(BTC) catalyst (1 mol%), TEA (1.1 mmol) and DCM at room temperature was found to be the best optimized reaction conditions to perform the coupling reactions.

With optimal reaction conditions, this methodology was extended to several coupling reactions with various substituted benzaldehydes and alkynes (Table 2). It is evident that nature and position of substituent on phenyl ring of the benzaldehyde did not affect the yield of the reaction. Both aromatic and aliphatic alkynes were given their desired product in excellent yields. All the products were characterized by NMR and mass spectral techniques.

Table 1: Screening of the reaction conditions[a]



Entry	Catalyst	Base	Solvent	Time (min)[b]	Yield (%)[c]
1	-	TEA	DCM	60	-
2	CuI	TEA	DCM	15	87
3	CuI	Pyridine	DCM	15	43
4	CuI	DIPEA	DCM	15	68
5	CuI	K_2CO_3	DCM	30	76
6	CuBr	TEA	DCM	20	67
7	CuCl	TEA	DCM	20	61
8	Cu(BTC)	TEA	$CHCl_3$	10	71
9	**Cu(BTC)[d]**	**TEA**	**DCM**	**5**	**95**
10	Cu(BTC)	DBU	ACN	5	32
11	Cu(BTC)	Cs_2CO_3	DCE	5	57
12	$Cu(OAc)_2.H_2O$	TEA	DCM	30	33
13	$Cu(NO_3)_2.3H_2O$	TEA	DCM	30	28
14	$Cu(SO_4)_2.5H_2O$	TEA	DCM	30	10
15	$Cu(OTf)_2$	TEA	DCM	30	13
16	$CuBr_2$	TEA	DCM	30	22
17	Cu_2O	TEA	DCM	30	15
18	Cu(BTC)	DABCO	THF	5	34
19	Cu(BTC)	TEA	Xylene	5	57
20	Cu(BTC)	TEA	Toluene	5	52
21	Cu(BTC)	TEA	1,4-Dioxane	5	44
22	Cu(BTC)	TEA	DMF	5	56
23	Cu(BTC)[e]	TEA	DCM	5	94
24	Cu(BTC)[f]	TEA	DCM	5	85

[a]Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), **3** (1 mmol), **4** (1 mmol), base (1.1 mmol), catalyst (1 mol%), solvent (3 mL), rt. [b]Reaction time was determined by monitoring disappearance of reactants on TLC. [c]Isolated yield. [d]1 mol% of catalyst was used. [e]5 mol% of catalyst was used. [f]0.5mol% of catalyst was used.

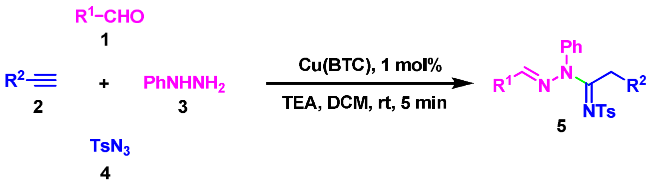
Recovery and Reusability of Cu(BTC) Catalyst

Heterogeneous nature of the solid catalyst was confirmed by reusability study for preparation of **5a**. The reaction was performed under optimized reaction conditions. After complete conversion of reactants, the reaction mixture was filtered to separate the solid catalyst. TLC was used to monitor the progress of the reaction. Recovered catalyst was washed with DCM and dried in air for 10 min prior to use for the next run. The catalyst was recovered in very high yield (96%).

The recovered catalyst was subjected to powder XRD and FT-IR analysis (Figure 2 & 3). A result of powder XRD and FT-IR spectrum indicates the crystalline nature of catalyst was intact even after several cycles of reactions. These results were also proved that the catalyst is remarkably heterogeneous. Deviation in the yield associated with the use of recycled catalyst is comparable to the yield obtained from reactions using fresh catalyst (Table 3). The catalyst was recovered and reused up to six times without any changes in the reaction time, yield and each run it was behaved as a fresh catalyst.

This methodology was scaled-up to 5g under standard conditions to afford **5a**. The desired product was obtained in 93% yield, which was in accordance with the yield obtained in the small scale reaction.

Table 2: Cu(BTC) catalysed synthesis of hydrazono-sulfonamide adducts: Scope with respect to aldehydes and alkynes[a]



Entry	**1** (R^1)	**2** (R^2)	**5** (Yield%)[b]	
1	4-MeC$_6$H$_4$ (**1a**)	Ph (**2a**)	**5a**	95
2	4-OMeC$_6$H$_4$ (**1b**)	**2a**	**5b**	93
3	4-CH(CH$_3$)$_2$C$_6$H$_4$ (**1c**)	**2a**	**5c**	93
4	2-OEtC$_6$H$_4$ (**1d**)	**2a**	**5d**	91
5	3-OMeC$_6$H$_4$ (**1e**)	**2a**	**5e**	90
6	2-OMeC$_6$H$_4$ (**1f**)	**2a**	**5f**	90
7	2,4-OMeC$_6$H$_3$ (**1g**)	**2a**	**5g**	87
8	4-EtC$_6$H$_4$ (**1h**)	**2a**	**5h**	94
9	C$_6$H$_5$ (**1i**)	**2a**	**5i**	92
10	4-MeSO$_2$C$_6$H$_4$ (**1j**)	**2a**	**5j**	88
11	4-FC$_6$H$_4$ (**1k**)	**2a**	**5k**	91
12	4-ClC$_6$H$_4$ (**1l**)	**2a**	**5l**	88
13	4-BrC$_6$H$_4$ (**1m**)	**2a**	**5m**	88
14	2-ClC$_6$H$_4$ (**1n**)	**2a**	**5n**	86
15	3-BrC$_6$H$_4$ (**1o**)	**2a**	**5o**	90
16	Biphenyl (**1p**)	**2a**	**5p**	89
17	Thienyl (**1q**)	**2a**	**5q**	89
18	1-Pyrenyl (**1r**)	**2a**	**5r**	80
19	9-Anthracenyl (**1s**)	**2a**	**5s**	81
20	**1b**	4-MeC$_6$H$_4$ (**2b**)	**5t**	89
21	**1m**	**2b**	**5u**	87
22	**1a**	4-*n*-pentylC$_6$H$_4$ (**2c**)	**5v**	90
23	**1a**	Cyclopropyl (**2d**)	**5w**	87

[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), **3** (1 mmol), **4** (1 mmol), TEA (1.1 mmol), Cu(BTC) (1 mol%), DCM (3 mL), rt, 5 min. [b] Isolated yield

Mechanism

Most of the azide-alkyne cycloaddition reactions were performed using homogeneous Cu(I) catalysts. A few reactions were reported in the literature utilizing heterogeneous Cu(I) or Cu(II) solid catalyst.[13] Yamaguchi et al[14] disclosed that Cu(II) hydroxide supported on alumina or titania is an efficient catalyst for azide-alkyne cycloaddition reactions. The mechanism suggests that, involvement of Cu(I)-acetylide intermediate which is formed during the reaction. It also proves that acetylene reduces Cu(II) to Cu(I) by induction method. Corma et al[15] reported that Cu-MOF's are efficient catalysts for ''click'' reactions. The authors thoroughly investigated the mechanism of the "click reaction" and hypothesized that Cu(II)-acetylide is formed during the course of reaction thus neglecting the Cu(I)-acetylide active species concept suggested by Yamaguchi et al[14]. Ketenimines are generated from *N*-sulfonyl triazole by base mediated ring opening isomerization. In Cu(BTC) MOF, the copper centers are in stable +2 oxidation state. To our surprise, no reports are available using Cu(II) catalysts to generate *N*-sulfonyl triazole, which is traditionally prepared from TsN$_3$ and alkynes catalyzed by Cu(I) salts.

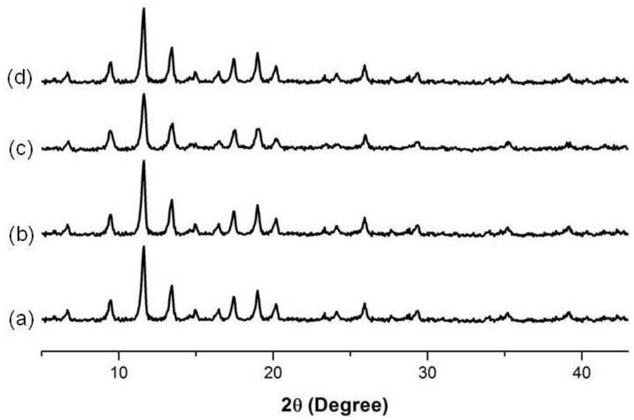


Figure 2. Powder XRD patterns of fresh and reused catalysts (a) Fresh, (b) 2nd run (c) 4th run (d) 6th run

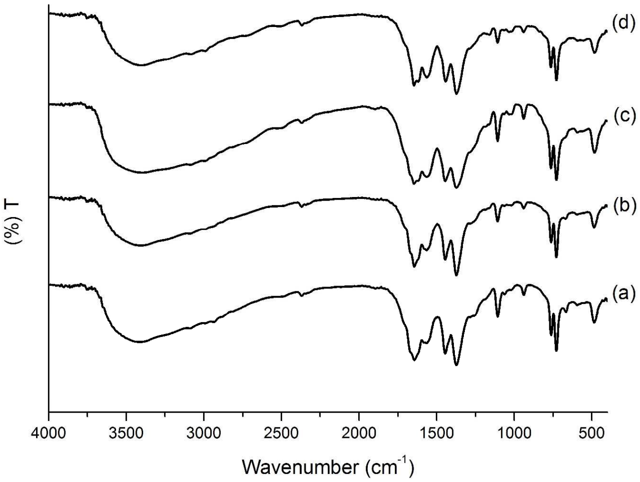


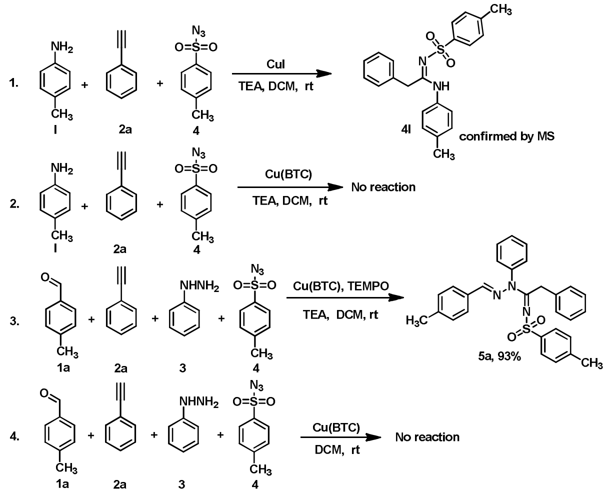
Figure 3. FT-IR spectra of fresh and reused catalysts (a) Fresh, (b) 2nd run (c) 4th run (d) 6th run

Table 3: Reusability of Cu(BTC) MOF[a]

Run	1st	2nd	3rd	4th	5th	6th
Yield[b]	95	93	95	94	90	91

[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), **3** (1 mmol), **4** (1 mmol), TEA (1.1 mmol), Cu(BTC) (1 mol%), DCM (3 mL), rt, 5 min. [b] Isolated yield

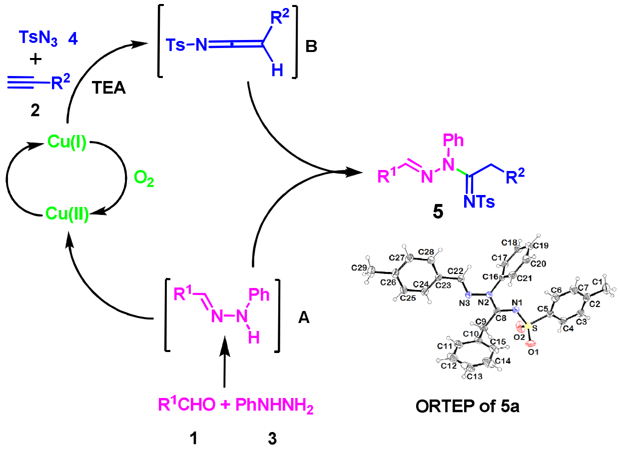
Based on the information obtained from the literatures, we performed few experiments to understand the mechanism of these coupling reactions. Chang et al[4a] disclosed three component coupling reactions of alkynes, azides, and amines using CuI as catalyst (Scheme 1, Reaction 1). The same reaction was performed in our laboratory using Cu(BTC) MOF as a catalyst (Scheme 1, Reaction 2). Surprisingly, no product was obtained (typical evolution of N$_2$ gas was not observed) and homo-coupled (1,3-diyne) products was also not obtained. To check the involvement of radical, we conducted the coupling reaction in the presence of 2,2,6,6-tetramethylpyridine *N*-oxide (TEMPO) as a radical scavenger (Scheme 1, Reaction 3). However, the desired product **5a** was obtained in 95% yield. Same yield was observed when the coupling reaction performed in the absence of TEMPO. The result of this experiment did not lead us to confirm the involvement of radical mechanism. The experiment performed in the absence of base (Scheme 1, Reaction 4) was not furnished any product indicating the ring opening rearrangement process of N-sulfonyl triazole did not take place.



Scheme 1. Control experiments

These results from the experiments led us to ignore alkyne as reductant[14] and to conclude that generated hydrazones and reactants play vital role in the mechanism. It must be noted that as soon as the base was added to the reaction mixture the typical effervescence due to evolution of nitrogen were observed. However, when amines were used instead of hydrazones, the evolution of nitrogen not noticed. This process was suggested that in situ formed hydrazones might have been reduced Cu(II) to Cu(I) species, and in turn initiates triazole formation by CuAAC, and regains its crystalline nature by air oxidation without affecting heterogeneity.

Based on the literatures and experiments performed by us, a plausible mechanistic pathway of these coupling reactions was outlined (Scheme 2**)**. The reaction of aldehyde-phenylhydrazine results in formation of hydrazone **A** which reduces Cu(II) to Cu(I), which in turn initiates triazole formation by CuAAC. This is followed by base mediated ring opening rearrangement to generate ketenimine intermediate **B**. Ketenimine **B** and hydrazone **A** coupled together to afford adduct **5**. It must be noted that the attempts to point out the formation of Cu(I) as an active species was unsuccessful.



Scheme 2. Proposed mechanistic cycle

Aggregation Induced Emission Enhancement (AIEE) study

Development of luminogens whose aggregates emits more efficiently than that in solution has aroused much interest in recent years. Tang's group in 2001 first reported that the luminescence of silole molecules was stronger in the aggregation state than that in the solution.[16] They coined ‘‘aggregation-induced emission enhancement’’ (AIEE) for this unusual phenomenon.[17] A variety of luminogens, including tetraphenylethene, silole, naphthalimide, indolo-carbazole and pyrene derivatives, were successively proved to have the same properties.[18] Such compounds were regarded as competitive candidates for practical use as highly emissive materials. Moreover, the introduction of functional groups into AIEE molecules will favor new development of chemo or biosensors for detecting metal cations, biomolecules and for cell imaging.[19] Inhibition of intramolecular rotations has been reported for the main reason for AIEE character of the luminogen. Recently, Pitchumani et al[5q] reported that the AIEE was aroused from inhibition of C=N isomerization at higher concentration of n-hexane. Based on the literatures, we anticipated that the prepared adducts could exhibit AIEE.

Initially, we screened the photophysical behaviour of all the adducts, among them **5r** shows remarkable AIEE character. Adduct **5r** is highly soluble in organic solvents but in-soluble in water. Absorption and emission properties of adduct **5r** are recorded by maintaining concentration at 1 × 10^{-5} M (Figure 4). Adduct **5r** is weakly fluorescent in pure THF solution but the moment water (90%) was added to the THF solution, it became slightly turbid and absorption bands was red shifted from 375 nm (0% water) to 425 nm (90% water).

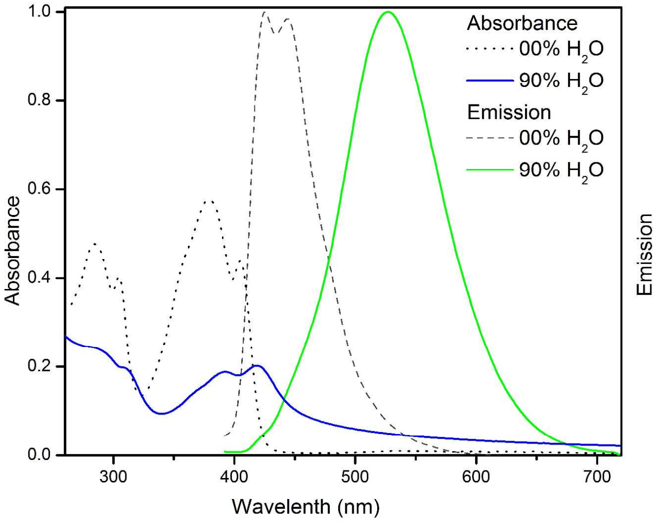


Figure 4. Normalized absorption and emission spectra of **5r**, 1 × 10^{-5} M

Encouraged by these results, photoluminescence (PL) spectrum was recorded in THF:Water solvent mixture with increasing concentration of water (Figure 5a). The PL intensity was gradually increased while increasing 10% of water by each time up 80%. Surprisingly, the peaks was significantly red shifted from 440 nm to 530 nm when 85% and 90% of water was added to THF and also, the THF:water mixture was turned to greenish-yellow under UV irradiation (see Supporting Information). These remarkable photophysical changes attributed to the inhibition of C=N isomerization at higher concentration of water, consequently the non-radiative decay from excited state gets suppressed and formation nano-aggregates. The formation of nano-aggregates was further confirmed by Transmission Electron Microscopy (TEM) analysis (Figure 5b).

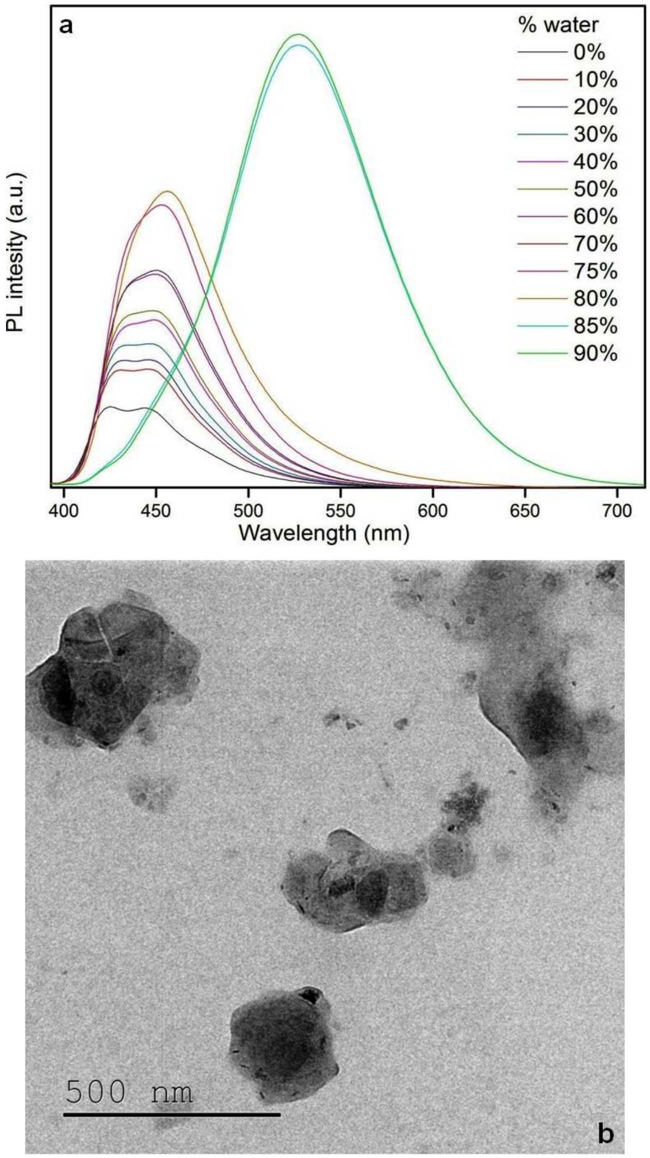


Figure 5. PL emission spectrum of **5r** (1×10^{-5} M) in THF–water mixtures (a), excitation wavelength 375 nm and TEM image of nano-aggregates for 90% water fraction (b).

The ground state geometry of the **5r** has been optimized using a density functional theory (DFT) method using B3LYP/6-31G basis sets. The DFT calculations were carried out using the Gaussian 09 program. The ground state optimized geometries and absorption behaviors of the corresponding transitions of the compounds were obtained from time dependant (TD) DFT using above mentioned functional and basis set. From the DFT results, the optimized structure of **5r** (Figure 6b) shows that the dihedral angle is 171.07. It is well clear that the adduct **5r** is in S-trans conformation. The frontier molecular orbital diagram shows that both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are mainly delocalized on whole π moiety and sulfonyl moiety (Figure 6a). The calculated energy gap between HOMO and LUMO is 3.00 eV.

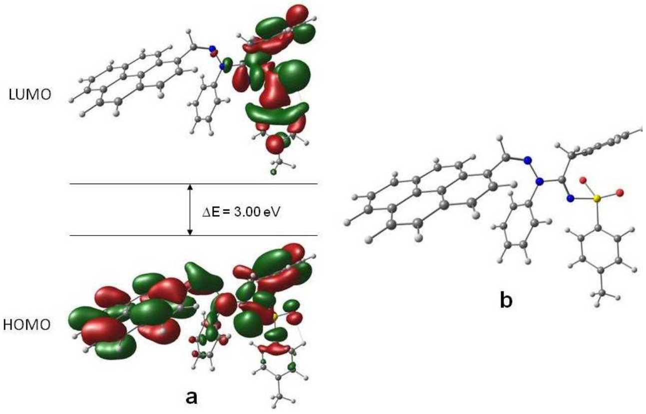


Figure 6. HOMO and LUMO energy levels of **5r** calculated by TD-DFT/B3LYP/6-31G basic sets (a) and optimized geometry of **5r** (b).

Conclusions

For the first time, Cu(II) MOF catalyzed four-component coupling reaction of aldehyde, alkyne, tosyl azide, and phenylhydrazine leading to hydrazono-sulfonamide adducts at room temperature was achieved. Merit of the present methodology is very simple experimental procedure, shorter reaction time, no column purification, easy isolation of product with excellent yield etc. Based on the control experiments, plausible mechanistic pathway was proposed. The heterogeneous Cu(II) catalyst was reused for six times without any deviation in the activity and reaction time. Adduct **5r** shows remarkable AIEE characteristics properties. Weakly fluorescent nature of **5r** in pure THF solution was finely tuned in aggregated state with remarkable red shift (90 nm) and the THF:water mixture was changed to greenish-yellow color under UV irradiation.TEM analysis confirms the formation of well defined nano-aggrregates. The observed photophysical changes were supported by DFT calculations. Further studies to determine the mechanism of these coupling reactions, synthetic and real time applications of the prepared adducts are under progress in our laboratory.

Experimental Section

Procedure for synthesis of Cu(BTC) MOF

Following the reported procedure[20], the Cu(BTC) MOF was prepared. A mixture of benzenetricarboxylic acid (BTC) (3 mmol) and $Cu(OAc)_2.H_2O$ (5.43 mmol) was stirred in a mixture of $DMF/EtOH/H_2O$ (1:1:1, 30 mL) at room temperature. To the clear solution obtained was added triethylamine (3.57 mmol). The reaction mixture was stirred for 23 h. The product formed was collected by filtration and washed with DMF (2 × 32 mL). It was dispersed in DCM (HPLC grade, 63 mL) overnight. Next day, the solvent was decanted and the solid was washed with fresh DCM (3 × 63 mL). It was then dried under vacuum at 130˚C for 12 h. Cu(BTC) MOF was obtained as deep blue colored solid in 47% yield. Thus obtained Cu(BTC) MOF was characterized using powder XRD and FT-IR techniques (see Supporting Information), results of which were in accordance with those reported by Yaghi et al.[20] In FT-IR spectra peak at 1760–1690 cm^{-1} corresponding to carboxylic acid was absent. Presence of strong peak at 1645 cm^{-1} corresponding to stretching frequency of carboxylate anions indicated that carboxylic acid groups in BTC underwent deprotonation. Powder XRD pattern confirmed that the material is highly crystalline in nature. The diffraction peaks of obtained Cu(BTC) MOF is consistent with the previous reports.[20, 21]

General procedure for Cu(BTC) MOF catalyzed four-component coupling reactions

To the stirring mixture of aldehyde **1** (1 mmol) and phenylhydrazine **3** (1 mmol) in DCM (3 mL) was added alkyne **2** (1 mmol), azide **4** (1 mmol) and activated Cu(BTC) MOF (1 mol%). To the above mixture, triethylamine (1.1 mmol) was added slowly. The whole reaction mixture was allowed agitated for 5 min at room temperature and then filtered to separate the catalyst from reaction mixture. To the filtrate was added petroleum ether and ethyl acetate mixture (1:1, 20 mL) and resulting mixture was stirred for 10 min. About 75% of solvent mixture was distilled off from filtrate under vacuum at 70 ˚C. The above crude product was cooled to 0 to 5 ˚C and triturated immediately in 5-8 min to afford white solid which was collected by filtration. The recovered catalyst was thoroughly washed with DCM and air dried for 10 min before using it for next reaction.

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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/

1 **For reviews in MCR's:** a) A. Dömling, W. Wang and K. Wang, *Chem. Rev.,* 2012, **112***,* 3083-3135; b) K. C. Nicolaou, D. J. Edmonds and P. G. Bulger, *Angew. Chem.,* 2006, **118***,* 7292-7344; *Angew. Chem. Int. Ed.,* 2006, 45, 7134-7186; (c) M. J. Climent, A. Corma and S. Iborra, *Chem. Rev.,* 2011, **111***,* 1072-1133; d) K. C. Nicolaou and J. S. Chen, *Chem. Soc. Rev.,* 2009, **38***,* 2993-3009; e) H. Bienayme, C. Hulme, G. Oddon and P. Schmitt, *Chem. − Eur. J.,* 2000, **6***,* 3321-3329; f) E. Ruijter, R. Scheffelaar and R. V. A Orru, *Angew. Chem. Int. Ed.,* 2011, **50***,* 6234-6246; g) A. Dömling, *Chem. Rev.,* 2006, **106***,* 17-89; (h) C. de Graaff, E. Ruijter and R. V. A. Orru, *Chem. Soc. Rev.,* 2012, **41***,* 3969-4009.

2 **For recent reviews:** a) J. E. Hein and V. V. Fokin, *Chem. Soc. Rev.,* 2010, **39***,* 1302-1315; b) P. Lu and Y. Wang, *Synlett*., 2010, **2***,* 165-173; c) E. J. Yoo and S. Chang, *Curr. Org. Chem.,* 2009, **13***,* 1766-1776; d) P. Lu and Y. G. Wang, *Chem. Soc. Rev.,* 2012, **41***,* 5687-5705; e) S. H. Kim, S. H. Park, J. H. Choi and S. Chang, *Chem. Asian J.*, 2011, **6***,* 2618-2634.

3 a) S. L. Cui, X. F. Lin and Y. G. Wang, *Org. Lett.,* 2006, **8***,* 4517-4520; b) J. Wang, J. Wang, Y. Zhu, P. Lu and Y. G. Wang, *Chem. Commun.,* 2011, **47***,* 3275-3277; c) W. Lu, W. Z. Song, D. Hong, P. Lu and Y. G. Wang, *Adv. Synth. Catal.,* 2009, **351***,* 1768-1772; d) W. Song, W. Lu, J. Wang, P. Lu and Y. G. Wang, *J. Org. Chem.,* 2010, **75***,* 3481-3483; e) S. L. Cui, J. Wang and Y. G. Wang, *Org. Lett.,* 2008, **10***,* 1267-1269; f) Y. Shen, S. Cui, J. Wang, X. Chen, P. Lu and Y. G. Wang, *Adv. Synth. Catal.,* 2010, **352***,* 1139-1144; g) H. Jin, X. Xu, J. Gao, J. Zhong and Y. G. Wang, *Adv. Synth. Catal.,* 2010, **352***,* 347-350; h) S. L. Cui, J. Wang and Y. G. Wang, *Org. Lett.,* 2007, **9***,* 5023-5025; i) Y. Li, D. Hong, Y. X. Zhu, P. Lu and Y. G. Wang, *Tetrahedron,* 2011, **67***,* 8086-8091; j) J. Wang, J. Wang, P. Lu and Y. G. Wang, *J. Org. Chem.,* 2013, **78***,* 8816-8820.

4 a) I. Bae, H. Han and S. Chang, *J. Am. Chem. Soc.,* 2005, **127***,* 2038-2039; b) E. J. Yoo, M. Ahlquist, I. Bae, K. B. Sharpless, V. V. Folkin and S. Chang, *J. Org. Chem.,* 2008, **73***,* 5520-5528; c) S. H. Cho, E. J. Yoo, I. Bae and S. Chang, *J. Am. Chem. Soc.,* 2005, **127***,* 16046-16047; d) E. J. Yoo, I. Bae, S. H. Cho, H. Han and S. Chang, *Org. Lett.,* 2006, **8***,* 1347-1350; e) S. H. Cho and S. Chang, *Angew. Chem. Int. Ed.,* 2007, **46***,* 1897-1900; f) S. H. Cho and S. Chang, *Angew. Chem. Int. Ed.,* 2008, **47***,* 2836-2839; g) E. J. Yoo and S. Chang, *Org. Lett.,* 2008, **10***,* 1163-1166; h) J. Kim, S. Y. Lee, J. Lee, Y. Do and S. Chang, *J. Org. Chem.,* 2008, **73***,* 9454-9457; i) E. J. Yoo, M. Ahlquist, S. H. Kim, I. Bae, V. V. Fokin, K. B. Sharpless and S. Chang, *Angew. Chem. Int. Ed.,* 2007, **46***,* 1730-1733; j) R. Husmann, Y. S. Na, C. Bolm and S. Chang, *Chem. Commun.,* 2010, **46***,* 5494-5496.

5 a) M. P. Cassidy, J. Raushel and V. V. Fokin, *Angew. Chem. Int. Ed.,* 2006, **45***,* 3154-3157; b) Y. Shang, X. He, J. Hu, J. Wu, M. Zhang, S. Yu and Q. Zhang, *Adv. Synth. Catal.,* 2009, **351***,* 2709-2713; c) W. Yao, L. Pan, Y. Zhang, G. Wang, X. Wang and C. Ma, *Angew. Chem. Int. Ed.,* 2010, **49***,* 9210-9214; d) K. Namitharan and K. Pitchumani, *Org. Lett.,* 2011, **13***,* 5728-5731; e) Z. Chen, C. Ye, L. Gao and J. Wu, *Chem. Commun.,* 2011, **47***,* 5623-5625; f) K. Namitharan and K. Pitchumani, *Adv. Synth. Catal.,* 2013, **355***,* 93-98; g) S. Li and J. Wu, *Chem. Commun.,* 2012, **48***,* 8973-8975; h) B.-S. Li, B.-M. Yang, S.-H. Wang, Y.-Q. Zhang, X.-P. Cao and Y.-Q. Tu, *Chem. Sci.,* 2012, **3***,* 1975-1979; i) G. Murugavel and T. Punniyamurthy, *Org. Lett.,* 2013, **15***,* 3828-3831; j) B. Bo Jiang, X. T Tu, X. Wang, S. J. Tu and G. Li, *Org. Lett.,* 2014, **16***,* 3656-3659; k) Z. Chen, D. Zheng and J. Wu, *Org. Lett.,* 2011, **13***,* 848-851; l) S. Periyaraja, P. Shanmugam and A. B. Mandal, *Eur. J. Org. Chem.,* 2014, 954-965; m) S. Li, Y. Luo and J. Wu, *Org. Lett.,* 2011, **13***,* 4312-4315; n) G. Cheng and X. Cui, *Org. Lett.,* 2013, **15***,* 1480-1483; o) Y. K. Kumar, G. R. Kumar and M. S. Reddy, *J. Org. Chem.,* 2014, **79***,* 823-828; p) X. Xu, D. Cheng, J. Li, H. Guo and J. Yan, *Org. Lett.,* 2007, **9***,* 1585-1587; q) K. Namitharan and K. Pitchumani, *Org. Biomol. Chem.,*2012, **10***,* 2937-2941.

6 **For reviews in MOF:** a) A. Corma, H. Garcia and F. X. L. Xamena, *Chem. Rev.,* 2010, **110***,* 4606-4655; b) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.,* 2009, **38***,* 1450-1459; c) S. Natarajan and P. Mahata, *Chem. Soc. Rev.,* 2009, **38***,* 2304-2318; d) D. Farrusseng, S. Aguado and C. Pinel, *Angew. Chem., Int. Ed.,* 2009, **48***,* 7502-7513; e) D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.,* 2009, **38***,* 1257-1283.

7 a) P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J. S. Chang, Y. K. Hwang, V. Marsaud, P. N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur and R. Gref, *Nat. Mater.,* 2010, **9***,* 172-178; b) S. M. Cohen, *Curr. Opin. Chem. Biol.,* 2007, **11***,* 115-120.

8 a) L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.,* 2009, **38***,* 1294-1314; b) S. Q. Ma and H. C. Zhou, *Chem. Commun.,* 2010, **46***,* 44-53; c) H. K. Chae, D. Y. Siberio-Perez, J. Kim, Y. B. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe and O. M. Yaghi, *Nature,* 2004, **427***,* 523-527.

9 a) M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez and G. Ferey, *J. Am. Chem. Soc.,* 2009, **131***,* 10857-10859; b) B. V. Harbuzaru, A. Corma, F. Rey, J. L. Jorda, D. Ananias, L. D. Carlos and J. Rocha, *Angew. Chem.,* 2009, **121***,* 6598-6601; *Angew. Chem. Int. Ed.,* 2009, **48***,* 6476-6479.

10 **Selected examples for MOF as catalyst:** a) S. Regati, Y. He, M. Thimmaiah, P. Li, S. Xiang, B. Chen and J. C. G. Zhao, *Chem.*

Commun., 2013, **49**, 9836-9838; b) J. Park, J. R. Li, Y. P. Chen, J. Yu, A. A. Yakovenko, Z. U. Wang, L. B. Sun, P. B. Balbuena and H. C. Zhou, *Chem. Commun.*, 2012, **48**, 9995-9997; c) S. Horike, M. Dinca, K. Tamaki and J. R. Long, *J. Am. Chem. Soc.*, 2008, **130**, 5854-5855; d) C. D. Nicola, Y. Y. Karabach, A. M. Kirillov, M. Monari, L. Pandolfo, C. Pettinari and A. J. L. Pombeiro, *Inorg. Chem.*, 2007, **46**, 221-230; e) X. Tan, L. Li, J. Zhang, X. Han, L. Jiang, F. Li and C. Y. Su, *Chem. Mater.*, 2012, **24**, 480-485; f) M. Almáši, V. Zeleňák, M. Opanasenko and J. Čejka, *Dalton Trans.*, 2014, **43**, 3730-3738; g) S. Gao, N. Zhao, M. Shu and S. Che, *Appl. Catal. A: General*, 2010, **388**, 196-201; h) M. A. Gotthardt, A. Beilmann, R. Schoch, J. Engelke and W. Kleist, *RSC Adv.*, 2013, **3**, 10676-1067;. i) J. Long, L. Wang, X. Gao, C. Bai, H. Jiang and Y. Li, *Chem. Commun.*, 2012, **48**, 12109-12111; j) F. Carson, S. Agrawal, M. Gustafsson, A. Bartoszewicz, F. Moraga, X. Zou and B. M. Matute, *Chem. − Eur. J.*, 2012, **18**, 15337-15344; k) A. Dhakshinamoorthy, M. Alvaro, H. Chevreau, P. Horcajada, T. Devic, C. Serre and H. Garcia, *Catal. Sci. Technol.*, 2012, **2**, 324-330; l) J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang and B. Han, *Green Chem.*, 2009, **11**, 1031-1036; m) X-W. Dong, T. Liu, Y. Z. Hu, X-Y. Liu and C-M. Che, *Chem. Commun.*, 2013, **49**, 7681-7683; n). L. Mitchell, B. G. Santiago, J. P. S. Mowat, M. E. Gunn, P. Williamson, N. Acerbi, M. L. Clarke and P. A. Wright, *Catal. Sci. Technol.*, 2013, **3**, 606-617.; o) Y. Huang, Z. Lin and R. Cao, *Chem. − Eur. J.*, 2011, **17**, 12706-12712.

11 **Selected examples for Cu-MOF catalyst:** a) D. Jiang, T. Mallat, F. Krumeich and A. Baiker, *J. Catal.*, 2008, **257**, 390-395; b) S. Priyadarshini, P. J. A. Joseph, M. L. Kantam and B. Sreedhar, *Tetrahedron*, 2013, **69**, 6409-6414; c) P. Puthiaraj, P. Suresh and K. Pitchumani, *Green Chem.*, 2014, **16**, 2865-2875; d) L. T. L. Nguyen, T. T. Nguyen, K. D. Nguyen and N. T. S Phan,. *Appl. Catal. A: General*, 2012, **425**, 44-52; e) A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *ACS Catal.*, 2011, **1**, 48-53; f) A. Arnanz, M. P. Sierra, A. Corma, M. Iglesias and F. Sanchez, *Adv. Synth. Catal.*, 2012, **354**, 1347-1355; g) N. T. S. Phan, T. T. Nguyen, C. V. Nguyen and T. T. Nguyen, *Appl. Catal. A: General*, 2013, **457**, 69-77; h) E. P. Mayoral and J. Ĉejka, *ChemCatChem*, 2011**,** **3**, 157-159; i) A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *J. Catal.*, 2009, **267**, 1-4.

12 S. Parshamoni, S. Sanda, H. S. Jena and S. Konar, *Dalton Trans*., 2014, **43**,7191–7199.

13 a) S. Chassaing, M. Kumarraja, A. S. S. Sido, P. Pale and J. Sommer, *Org. Lett*., 2007, **9**, 883-886; b). T. Katayama, K. Kamata, K. Yamaguchi and N. Mizuno, *ChemSusChem*, 2009, **2**, 59-62; c) I. S. Park, M. S. Kwon, Y. Kim, J. S. Lee and J. Park, *Org. Lett*., 2008, **10**, 497-500; d) J. C. Park, A. Y. Kim, J. Y. Kim, S. Park, K. H. Park and H. Song, *Chem. Commun.*, 2012, **48**, 8484-8486; e) L. D. Pachón, J. H. V. Maarseveen and G. Rothenberg, *Adv. Synth. Catal.*, 2005, **347**, 811-815; f) K. Namitharan, M. Kumarraja and K. Pitchumani, *Chem. − Eur. J.*, 2009, **15**, 2755-2758; g) R. B. N. Baig and R. S. Varma, *Green Chem*., 2012, **14**, 625-632; h) M. Liu and O. Reiser, *Org. Lett.*, 2011, **13**, 1102-1105; i) Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, *J. Am. Chem. Soc.*, 2012, **134**, 9285-9290; j) J. A. Shin, K. H. Lee and Y. G. Lim, *J. Org. Chem.*, 2012, **77**, 4117-4122; k) J. Y Kim, J. C. Park, H. Kang, H. Song and K. H. Park, *Chem. Commun.*, 2010, **46**, 439-441.

14 K. Yamaguchi, T. Oishi, T. Katayama and N. Mizuno, *Chem. − Eur. J.*, 2009, **15**, 10464-10472.

15 I. Luz, F. X. L. Xamena and A. Corma, *J. Catal.*, 2010, **276**, 134-140.

16 J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun*., 2001, 1740-1741.

17 a) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011,**40**, 5361–5388; b) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun*., 2009, 4332–4353; c) J. Mei, Y. Hong, J. W. Y. Lam, A. Qin, Y, Tang and B. Z. Tang, *Adv. Mater.*, 2014, **26**, 5429–5479.

18 a) B. Chen, Y. Jiang, B. He, J. Zhou, H. H. Y. Sung, I. D. Williams, P. Lu, H. S. Kwok, H. Qiu, Z. Zhao and B. Z. Tang, *Chem. Asian J.*, 2014, **9**, 2937 – 2945; b) W. Z. Yuan, P. Lu, S. Chen, J. W. Y. Lam, Z. Wang, Y. Liu, H. S. Kowk, Y. Ma and B. Z. Tang, *Adv. Mater.*, 2010, **22**, 2159–2163; c) Z. J. Zhao, S. M. Chen, J. W. Y. Lam, Z. M. Wang, P. Lu, F. Mahtab, H. H. Y. Sung, I. D. Williams, Y. G. Ma, H. S. Kwok and B. Z. Tang, *J. Mater. Chem.*, 2011, **21**, 7210–7216; d) W. B. Jia, H. W. Wang, L. M. Yang, H. B. Lu, L. Kong, Y. P. Tian, X. T. Tao and J. X. Yang, *J. Mater. Chem. C*, 2013, **1**, 7092–7101; e) S. Mukherjee and P. Thilagar, *Chem. − Eur. J.*, 2014, **20**, 9052 – 9062; f) S. Mukherjee and P. Thilagar, *Chem. − Eur. J.*, 2014, **20**, 8012 – 8023; g) J.Zhou, Z. Chang, Y. Jiang, B. He, M. Du, P. Lu, P. Lu, H. S. Kwok, A. Qin, H. Qiu, Z. Zhao and B. Z. Tang *Chem. Commun.*, 2013,**49**, 2491—2493; h) P. Y. Gu, C.J. Lu, F. L. Ye, J. F. Ge, Q. F. Xu, Z. J. Hu, N. J. Li and J. M. Lu *Chem. Commun.*, 2012,**48**, 10234–10236; i) Z. Zhao, P. Lu, J. W. Y. Lam, Z. Wang, C. Y. K. Chan, H. H. Y. Sung, I. D. Williams, Y. Ma and B. Z. Tang, *Chem. Sci.*, 2011, **2**, 672–675.

19 a) T. Sanji, K. Shiraishi, M. Nakamura and M. Tanaka *Chem. Asian J.*, 2010, **5**, 817 – 824; b) D. Tong, H. Duan, J. Wang, Z. Yang and Y. Lin, *Sensors and Actuators B*, 2014, **195**, 80–84; c) Q. Zhao, K. Li, S. Chen, A. Qin, D. Ding, S. Zhang, Y. Liu, B. Liu, J. Z. Sun and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 15128–15135; d) H. H. Lin, Y. C. Chan, J. W. Chen and C. C. Chang, *J. Mater. Chem.*, 2011, **21**, 3170–3177; e) E. Wang, E. Zhao, Y. Hong, J. W. Y. Lam and B. Z. Tang, *J. Mater. Chem. B*, 2014, **2**,2013–2019.

20 D. J. Tranchemontagne, J. R. Hunt and O. M. Yaghi, *Tetrahedron*, 2008, **64**, 8553-8557.

21 K. Schlichte, T. Kratzke and S. Kaskel, *Micropor. Mesopor. Mater.*, 2004, **73**,81-88.

One-Pot Synthesis of Hydrazono-Sulfonamide Adducts using Cu(BTC) MOF Catalyst and Their Remarkable AIEE Properties: Unprecedented Copper(II)-Catalyzed Generation of Ketenimine

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TOC Graphical Abstract