Oxidative cyclization of *N*-acylhydrazones. Development of highly selective turn-on fluorescent chemodosimeters for Cu^{2+}†

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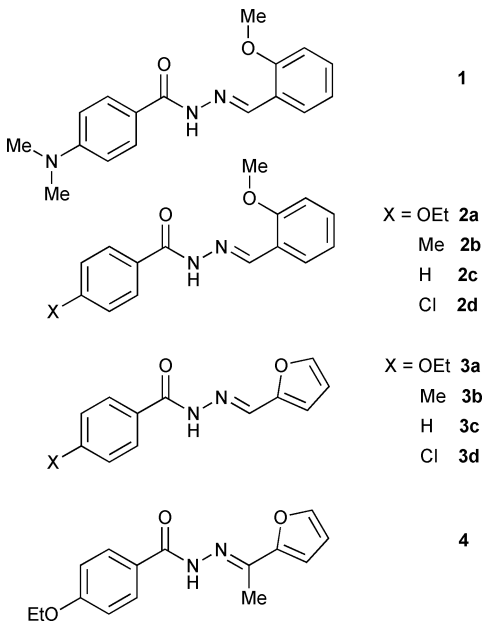
A series of *N*-acylhydrazones were synthesised and found to be "turn-on" fluorescent chemodosimeters for Cu^{2+}. Among the tested transition metal ions such as Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Ni^{2+}, a prominent fluorescence enhancement of up to 1000-fold was only observed for Cu^{2+} in acetonitrile (CH_3CN). This was indicated by an onset of unprecedented structured emission. Detailed experiments established that the highly Cu^{2+} selective fluorescence enhancement resulted from an oxidative cyclization by Cu^{2+} of the originally nonfluorescent *N*-acylhydrazones into highly fluorescent rigid 1,3,4-oxadiazoles, *n*-dope type blocks in optoelectronic materials. The chemodosimeters can be applied to sense Cu^{2+} at nM levels in CH_3CN and sub-μM levels in neutral aqueous environments, despite a slower response in the latter case. It is expected that these redox-based chemodosimeters might be of general applicability.

Introduction

N-Acylhydrazones have been widely employed in organic[1] and analytical[2] chemistry, mainly in terms of metal ligands.[2,3] It is known that *N*-acylhydrazones coordinate strongly with a variety of transition metal ions, forming complexes of varied biological and pharmaceutical activities. The development of sensitive and selective fluorescent chemosensors for biologically important metal ions is of intense current interest because these metal ions play important roles in living and environmental systems.[4] Special attention has been focused on the design of fluorescent chemosensors for Cu^{2+} due to its essential yet toxic nature.[5] We previously found that *N*-(*p*-dimethylaminobenzoyl)hydrazone (**1**, Scheme 1), bearing an intramolecular charge transfer (ICT) fluorophore, *p*-dimethylaminobenzamide, showed a highly selective fluorescence response toward Cu^{2+} in CH_3CN, despite similar absorption spectral variations being observed with other metal ions such as Pb^{2+}, Zn^{2+}, and Hg^{2+} too.[6] This finding suggested that the *N*-acylhydrazone in this case might act not only as a ligand. Although several explanations were proposed, the exact mechanism, however, could not be clarified with just one molecule that also bears complicated excited-state ICT photophysics.[6] In order to understand the responding mechanism, we decided to remove the ICT channel in **1** to simplify the excited-state photophysics and data rationalization. We therefore extended our investigation to a variety of *N*-benzoylhydrazones **2** and **3** bearing substituents X less electron-donating than *p*-NMe_2 in **1** (Scheme 1). A highly selective fluorescence response toward Cu^{2+} was again observed in both CH_3CN and CH_3CN–H_2O solutions.



Scheme 1 Molecular structures of *N*-acylhydrazones **1**–**4**.

In particular, the observed enhanced emission is unprecedentedly structured in these polar solvents. Detailed experiments allowed us to establish that the enhanced fluorescence was due to an oxidative cyclization by Cu^{2+} of the originally nonfluorescent *N*-acylhydrazones into highly fluorescent rigid 1,3,4-oxadiazoles. *N*-Acylhydrazones were therefore shown to be a kind of redox-based "turn-on" fluorescent chemodosimeter for Cu^{2+}, a new entrance to the active subject of "turn-on" fluorescent chemosensors for Cu^{2+}, a strongly quenching paramagnetic species.[7–9] It should be pointed out that there have been several nice Cu^{2+} chemodosimeters with enhanced fluorescence signal outputs, which however follow hydrolysis[8] or rearrangement reactions.[9]

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Results and discussion

N-Acylhydrazones **2** and **3** were facilely synthesized by a simple one-step reaction in ethanol of the corresponding *N*-benzoylhydrazine with 2-methoxybenzaldehyde and furan-2-carbaldehyde, respectively. **2a** in CH_3CN exhibits three absorption bands centred at 287, 298, and 323 nm with respective molar absorption coefficients of 2.67×10^4, 2.59×10^4, and 2.93×10^4 M^{-1} cm^{-1}, indicative of the (π, π^*) transition character. In the presence of Cu^{2+}, the band at 323 nm is attenuated and a shoulder at *ca.* 365 nm is developed (Fig. 1a). Hg^{2+} and Pb^{2+} exert a similar effect, whereas other heavy transition metal ions such as Zn^{2+}, Cd^{2+}, and Ni^{2+} exert a minor influence on the absorption spectrum. **2b–d** behave similarly in their absorption spectral response toward these metal ions (Fig. S1-S4†). **3**, analogues of **2**, exhibit spectral variation profiles (Fig. S5-S8†) similar to those of **2**. **2** and **3** in CH_3CN emit extremely weak fluorescence. In the presence of Cu^{2+}, however, an instant response was observed by a dramatic enhancement of up to 1000-fold, despite the well-known quenching character of Cu^{2+} (Fig. 1b, 2, S9, and S10†). The fluorescence response profiles of **2** and **3** toward Cu^{2+} were found to be simpler than that of **1**,[6] in that there was no emission band shift and no fluorescence quenching at higher Cu^{2+} concentration with **2** and **3** (Fig. 2). Removing the excited-state ICT channel in **1**, much higher fluorescence enhancement for **2a** and **3a** by Cu^{2+} was observed (Fig. 2) than that for **1** which was *ca.*180-fold.[6] Assays of the fluorescence response of **2** and **3** in CH_3CN toward a variety of other transition metal ions such as Pb^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Ni^{2+} indicated that a prominent fluorescence enhancement was again only observed for Cu^{2+} whereas the other transition metal ions tested exerted little influence (Fig. 2). This means that the fluorescence responses of **2** and **3** are highly selective for Cu^{2+}, as is **1**.[6] The fluorescence enhancement factors (FEFs) of **2** and **3** by Cu^{2+} were found to be higher with increasing electron-donating ability of the substituent X and the FEFs of **3** were much higher than those of **2** (Fig. 2 and Table 1). It therefore appears that higher electron density at the hydrazone moiety and the relatively more exposed furan oxygen atom in **3** are important for higher FEFs. The fact that the fluorescence in CH_3CN of **4** (Scheme 1), a control molecule for **3a**, does not show any response toward Cu^{2+}, despite a substantial absorption variation (Fig. 3), nicely indicates that the vinyl proton =C*H* in **3a** plays an essential role in the fluorescence enhancement of **3a** by Cu^{2+}.

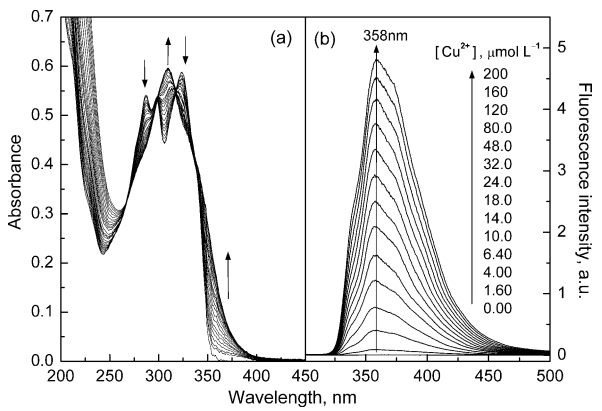


Fig. 1 Absorption (a) and fluorescence (b) spectra of **2a** (20 μM) in CH_3CN in the presence of increasing concentrations of Cu^{2+} (0–200 μM). The excitation wavelength was 267 nm, an isosbestic wavelength observed in absorption titrations.

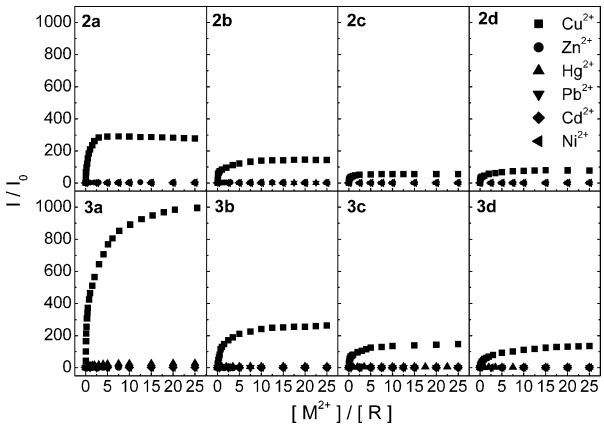


Fig. 2 Plots of fluorescence enhancement factor (FEF, I/I_0) in CH_3CN *versus* concentration ratio of metal ion to **2** and **3**. R = **2a–d** or **3a–d**, [**2**] = [**3**] = 10 μM.

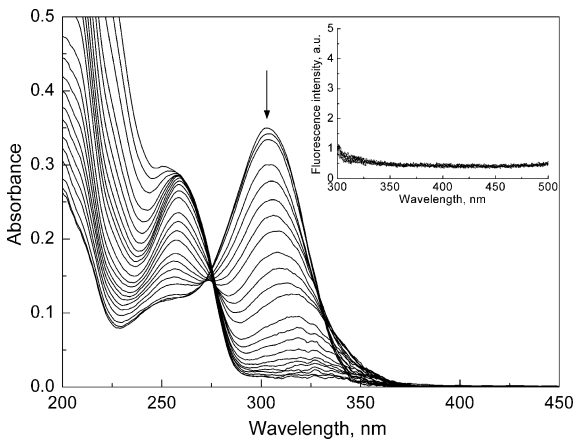


Fig. 3 Absorption spectra of **4** (10 μM) in CH_3CN in the presence of increasing concentrations of Cu^{2+} (0–200 μM). The excitation wavelength for acquiring fluorescence spectra given in the inset is an isosbestic wavelength of 274 nm.

It was surprising that an unexpected structured emission was observed for **2** and **3** in the presence of Cu^{2+} (Fig. 1b and 4). The trend shown in Fig. 4, that the emission becomes less structured while the FEF becomes lower with decreasing electron-donating ability of the substituent X, seems to suggest that the FEF value is related to the structured extent of the fluorescence spectrum. In order to test this correlation, an extended variety of *N*-acylhydrazones (**5–12**, Scheme 2) were prepared and their fluorescence response toward Cu^{2+} was monitored in CH_3CN. The fluorescence of **5–12** was similarly found to be enhanced by Cu^{2+}, confirming that *N*-acylhydrazones could in general act as an excellent family of "chemosensors" for Cu^{2+}. The structured extents of the emission spectra and the FEF values shown in Fig. 5, however, indicate that the apparent correlation between the structured extents and the FEF values reached in Fig. 4 does not hold in general, the rigidity of the ligand itself obviously contributing to the structured extent of the final emission spectrum. The unexpected structured

Table 1 Absorption and fluorescence spectral parameters of **2** and **3**, and **2** and **3** in the presence of 25 equivalents of metal ion in CH_3CN

	λ_{abs}/nm	$\varepsilon/10^4$ M^{-1} cm^{-1}	λ_{flu}/nm	FEF [a]	Φ [b]
2a	287/298/323	2.67/2.59/2.93	369	—	0.0007
2a + Ni^{2+}	365	0.32	364	1.9	0.0008
2a + Cu^{2+}	365	0.50	358	280	0.34
2a + Zn^{2+}	365	0.10	360	5.7	0.0013
2a + Cd^{2+}	364	0.08	367	1.4	0.0009
2a + Hg^{2+}	368	0.56	364	1.5	0.0025
2a + Pb^{2+}	375	0.26	364	1.4	0.0012
2b	286/297/323	2.12/2.10/2.50	370	—	0.0008
2b + Ni^{2+}	365	0.25	358	1.1	0.0010
2b + Cu^{2+}	368	0.33	351	140	0.30
2b + Zn^{2+}	365	0.10	353	5.7	0.0013
2b + Cd^{2+}	366	0.04	370	1.1	0.0010
2b + Hg^{2+}	372	0.40	357	2.4	0.0018
2b + Pb^{2+}	375	0.39	355	1.4	0.0011
2c	286/298/323	1.92/1.92/2.37	370	—	0.0007
2c + Ni^{2+}	364	0.20	358	1.1	0.0011
2c + Cu^{2+}	370	0.30	355	55	0.20
2c + Zn^{2+}	364	0.05	358	1.9	0.0027
2c + Cd^{2+}	364	0.05	370	2.2	0.0012
2c + Hg^{2+}	361	0.47	357	1.7	0.0024
2c + Pb^{2+}	375	0.50	357	1.3	0.0015
2d	287/299/324	1.74/1.71/2.10	370	—	0.0008
2d + Ni^{2+}	364	0.23	364	1.1	0.0010
2d + Cu^{2+}	365	0.41	362	80	0.26
2d + Zn^{2+}	366	0.10	364	1.9	0.0014
2d + Cd^{2+}	367	0.03	373	2.2	0.0011
2d + Hg^{2+}	364	0.50	363	1.7	0.0042
2d + Pb^{2+}	375	0.75	364	1.3	0.0015
3a	254/310	1.01/3.75	370	—	0.0004
3a + Ni^{2+}	315/378	2.94/0.51	367	1.4	0.0016
3a + Cu^{2+}	296/345	2.66/1.55	366	1000	0.49
3a + Zn^{2+}	326	3.76	365	5.2	0.0038
3a + Cd^{2+}	328	4.06	381	1.5	0.0024
3a + Hg^{2+}	338	4.15	368	29	0.0032
3a + Pb^{2+}	333	3.69	367	1.1	0.0034
3b	238/308	1.02/3.37	371	—	0.0004
3b + Ni^{2+}	310/365	3.10/0.23	358	1.1	0.0032
3b + Cu^{2+}	327	1.71	361	260	0.36
3b + Zn^{2+}	313	3.23	364	1.3	0.0018
3b + Cd^{2+}	319	3.31	379	1.1	0.0025
3b + Hg^{2+}	333	3.43	364	8.1	0.0047
3b + Pb^{2+}	330	3.22	366	1.1	0.0025
3c	228/308	0.94/3.01	370	—	0.0005
3c + Ni^{2+}	309/365	3.03/0.24	372	1.1	0.0029
3c + Cu^{2+}	319	1.01	360	145	0.33
3c + Zn^{2+}	311	2.87	372	1.2	0.0030
3c + Cd^{2+}	314	2.95	385	1.1	0.0007
3c + Hg^{2+}	332	3.07	365	6.3	0.0047
3c + Pb^{2+}	330	2.74	366	1.1	0.0038
3d	236/309	1.27/3.26	371	—	0.0004
3d + Ni^{2+}	310/371	2.92/0.29	370	1.1	0.0024
3d + Cu^{2+}	319/376	1.31/0.12	368	136	0.29
3d + Zn^{2+}	311/374	3.11/0.06	369	1.0	0.0017
3d + Cd^{2+}	314	3.15	396	1.0	0.0010
3d + Hg^{2+}	334/390	3.11/0.18	371	2.9	0.0039
3d + Pb^{2+}	332	2.88	372	1.1	0.0026

[a] Fluorescence enhancement factor, the ratio of the intensity of **2** and **3** in the presence of 25 equivalents of metal ion to that in the absence of metal ion. [b] Fluorescence quantum yields of **2** and **3**, and **2** and **3** in the presence of 25 equivalents of metal ion were measured using quinine sulfate as a standard (0.546 in 0.5 M H_2SO_4: Demas, J. N.; Crobys, G. A., *J. Phys. Chem.* **1971**, *75*, 991–1024). The measurement errors were up to 50% and 15% for *N*-acylhydrazones and their metal complexes, respectively.

emission and the high selectivity for Cu^{2+} therefore could not be simply attributed to Cu^{2+} coordination to *N*-acylhydrazones.

The fluorescence emission of a ligand can in principle be affected not only by metal ion coordination, but by a metal ion involved reaction as well.[10] The fact that the enhancement by Cu^{2+} of the fluorescence of **2** and **3** becomes higher when the substituent X is more electron-donating suggested that a redox reaction might occur. Indeed, it was reported that *N*-acylhydrazones underwent oxidative cyclization to 1,3,4-oxadiazoles by several oxidants.[11] $Cu(ClO_4)_2$ in CH_3CN could be an effective oxidant,

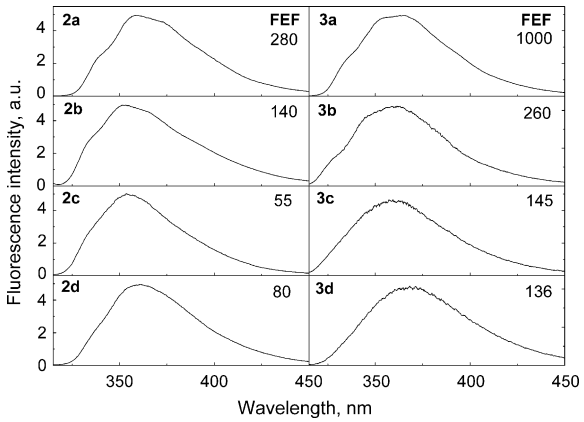


Fig. 4 Normalized fluorescence spectra of **2** and **3** in the presence of 25 equivalents of Cu^{2+} in CH_3CN at 25 °C.

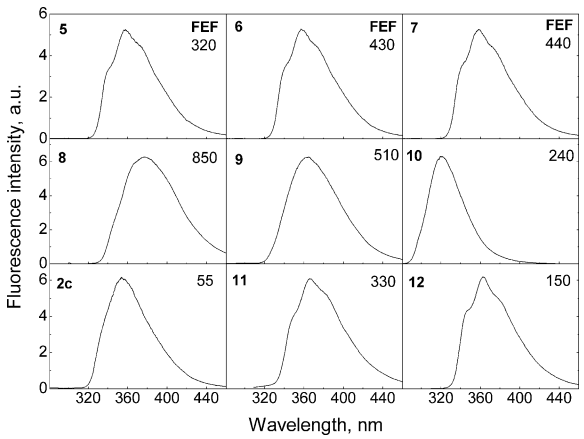
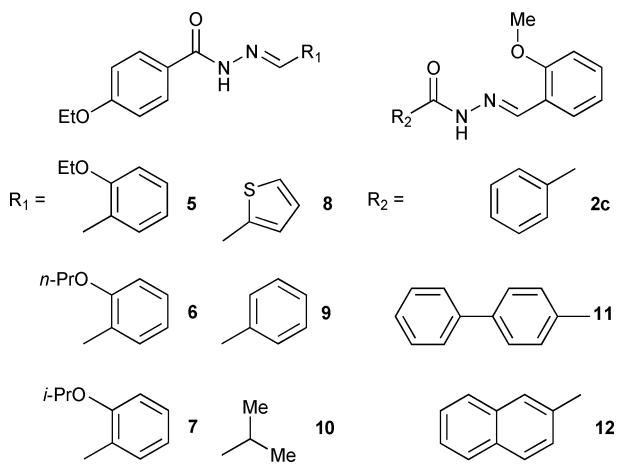


Fig. 5 Normalized fluorescence spectra of **2c** and **5–12** and FEF values in the presence of 25 equivalents of Cu^{2+} in CH_3CN at 25 °C.



Scheme 2 Structures of the extended variety of *N*-acylhydrazones.

since the Cu^{2+}/Cu^{+} couple in CH_3CN reportedly has a high reduction potential due to the stabilization of Cu^{+} by solvent coordination.[12] We therefore hypothesized that Cu^{2+} acted as an oxidant in CH_3CN to result in an oxidative cyclization of *N*-acylhydrazones into 1,3,4-oxadiazoles. As no credible signals were detected in the cyclic voltammograms of the reported *N*-acylhydrazones in CH_3CN, we were unable to directly confirm this hypothesis on the basis of redox potentials data. Alternatively, crucial evidence supporting this hypothesis was obtained from the independent syntheses of 1,3,4-oxadiazoles by reactions of *N*-acylhydrazones **3** with $Cu(ClO_4)_2$ in CH_3CN. The oxidative cyclization products 1,3,4-oxadiazoles **13** (Scheme 3, Table S1†) were fully characterized by HRMS, ^{1}H NMR, and ^{13}C NMR. Fluorescence excitation and emission spectra of the synthesized oxidative cyclization product **13a** were found identical to those of **3a** in the presence of 1.0 equivalent of Cu^{2+} (Fig. S11†). Obviously the observed fluorescence enhancement of **3a** by Cu^{2+} was not caused by Cu^{2+} coordination but instead by the oxidative cyclization reaction. In order to confirm the role of Cu^{2+} in the reaction of *N*-acylhydrazones in CH_3CN, EPR experiments in CH_3CN at 100 K were carried out in which the Cu^{2+} concentration was made constant while the **3a** concentration varied. It was found that the EPR signal of Cu^{2+} was indeed attenuated with increasing **3a** concentration (Fig. 6). This points to the conversion of Cu^{2+} into diamagnetic Cu^{+} that can be stabilized in CH_3CN. A mechanism of the oxidative cyclization by Cu^{2+} was therefore suggested (Scheme 3), which forms the basis of this new kind of redox-based chemodosimeter for Cu^{2+}.

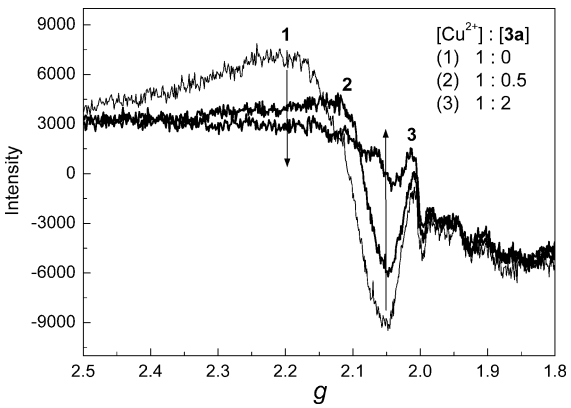
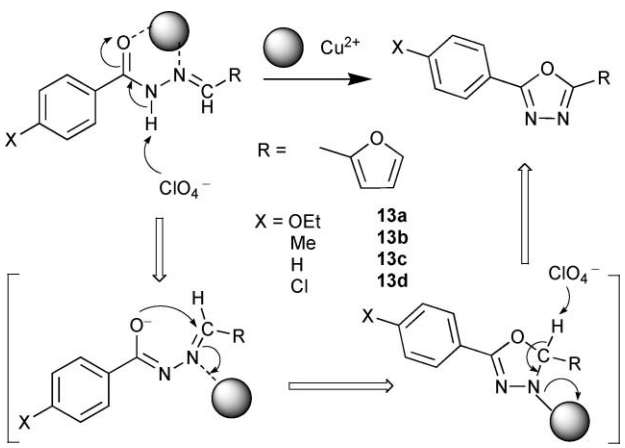


Fig. 6 EPR spectra of 1.0 mM Cu^{2+} in CH_3CN at 100 K with increasing concentration of **3a**.



Scheme 3 Proposed oxidative cyclization of *N*-acylhydrazones by Cu^{2+} in CH_3CN.

The absorption and fluorescence spectra of the oxidative cyclization product **13a** in CH_3CN, hardly changed upon the addition of

up to 25 equivalents Cu^{2+} (Fig. S12†). This explained the observed level-off of FEFs of **2** and **3** at higher Cu^{2+} concentration (Fig. 2). The observation that the absorption spectrum of **4** in CH_3CN undergoes substantial variation whereas it remains nonfluorescent in the presence of Cu^{2+} (Fig. 3) suggests that a simple coordination of Cu^{2+} to *N*-acylhydrazones in the ground state does not lead to an enhancement in the fluorescence of *N*-acylhydrazones. It was found that the fluorescence quantum yield of **13a** ($\Phi = 0.725$) in CH_3CN is *ca.*1800-fold that of **3a** ($\Phi = 4 \times 10^{-4}$). It is hence made clear that the dramatic fluorescence enhancement results fully from the oxidative cyclization by Cu^{2+} in CH_3CN of the nonfluorescent *N*-acylhydrazones which leads to the highly fluorescent rigid 1,3,4-oxadiazoles. The fluorescence response selectivity for Cu^{2+} is therefore due to its oxidation capability in CH_3CN, which makes it differ from the other metal ions tested. Hence the herein reported *N*-acylhydrazones do not act as metal coordinating chemosensors but instead fluorescent chemodosimeters for Cu^{2+}.

The high fluorescence enhancement factor of **3a** upon the addition of Cu^{2+} in CH_3CN shows great potential for application to the fluorescent sensing of Cu^{2+} at a low concentration level. The fluorescence of **3a** (0.5 μM) in the presence of 0.5 equivalents of Cu^{2+} levels off rapidly within 2 min (Fig. S13†). Fluorescence titration of **3a** (0.5 μM) shows a linear response toward Cu^{2+} over 25.0 nM to 0.25 μM in CH_3CN, with a detection limit of 3.5 nM (Fig. S14†). The fluorescent sensing of Cu^{2+} by **3a** in H_2O–CH_3CN solutions was also tested. The optimal conditions obtained for the assay (Fig. S15-S17†) were to carry it out in a 20:80 (v/v) mixture of CH_3CN and H_2O at pH 7.2 (5 mM Tris-HCl buffer, 0.1 M KCl) after heating at 50 °C for 3 h. In this case the detection limit was 0.30 μM. The FEF was proportional to the Cu^{2+} concentration over 1.0–160 μM at a **3a** concentration of 10 μM (Fig. 7). The fluorescence enhancement of **3a** by Cu^{2+} was also found to be independent of the counter anions of the Cu^{2+} such as NO_3^-, Cl^-, AcO^-, ClO_4^-, and SO_4^{2-} in aqueous CH_3CN solutions (Fig. S18†).

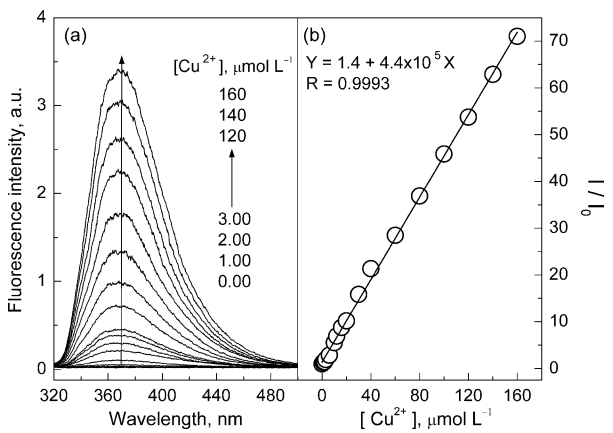


Fig. 7 (a) Fluorescence spectra of **3a** (10 μM) in a mixture of CH_3CN and Tris-HCl (5 mM, pH 7.2, 0.1 M KCl) aqueous buffer solution (20/80, v/v) in the presence of increasing concentrations of Cu^{2+} and (b) linear response curve. The excitation wavelength was 283 nm.

The fluorescence of **3a** in 80% H_2O–CH_3CN (v/v) was found to be hardly altered by the other metal ions tested: Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mg^{2+}, Ca^{2+}, and Ba^{2+}. The selectivity for Cu^{2+} over these metal ions remains remarkably high and the FEF of Cu^{2+} is only slightly influenced by the addition of either 5 equivalents of each or all of the interference metal ions, Fig. 8. In aqueous solutions, however, the response reaction was substantially slowed down, likely due to the efficient hydration of Cu^{2+}. Means of dehydrating Cu^{2+} and/or the stabilizing of Cu^+ in aqueous solutions are expected to enhance the reaction to a reasonable level that might allow efficient aqueous phase assays. This is currently underway in this laboratory.

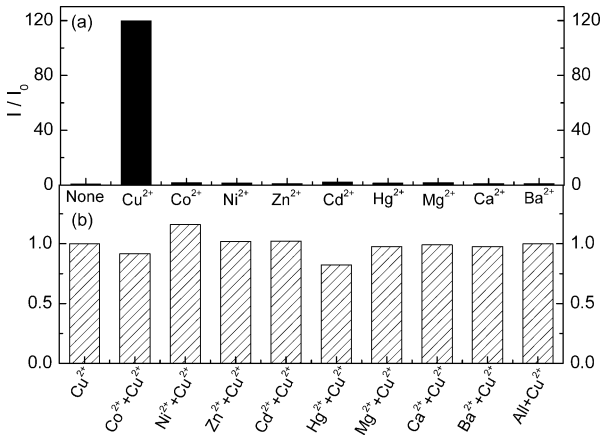


Fig. 8 (a) Fluorescence enhancement factors of **3a** with individual ions (2.5 mM) and (b) Relative fluorescence responses to Cu^{2+} (100 μM) plus interference metal ion (500 μM) in a mixture of CH_3CN and Tris-HCl (5 mM, pH 7.2, 0.1 M KCl) aqueous buffer solution (20/80, v/v). "All" means the relative fluorescence response of **3a** to Cu^{2+} (100 μM) plus all the interference metal ions tested, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mg^{2+}, Ca^{2+}, and Ba^{2+} at 500 μM each.

Conclusions

Highly selective and dramatic enhancements by Cu^{2+} of the fluorescence in CH_3CN and CH_3CN–H_2O of a variety of *N*-acylhydrazones were observed and were shown to result from an oxidative cyclization by Cu^{2+} of the originally nonfluorescent *N*-acylhydrazones to the highly fluorescent rigid 1,3,4-oxadiazoles. In agreement with this conclusion was the structured emission from the CH_3CN solution of *N*-acylhydrazones and Cu^{2+}. To the best of our knowledge, this is the first-set of reported chemodosimeters following an oxidative cyclization reaction that exhibits outstanding selectivity for Cu^{2+} with a dramatic fluorescence enhancement output. The chemodosimeters can be applied to sense Cu^{2+} at nanomolar levels in CH_3CN. Both high selectivity and sensitivity over other metal ions tested were obtained in a 20:80 (v/v) mixture of CH_3CN and Tris-HCl aqueous buffer solution, despite a much slower reaction rate. Although at the moment we are unable to set a structural limit for an *N*-acylhydrazone to be facilely oxidized by Cu^{2+}, as all those reported here undergo efficient oxidation cyclization, we expect that this oxidative cyclization reaction could be taken as an alternative route to 1,3,4-oxadiazoles, efficient electron acceptors employed in optoelectronic materials.[13] As redox reactions are easily made selective for a reductant or an oxidant and even made reversible, creating chemodosimeters following the redox reaction strategy illustrated here shall be of general applicability.

Experimental

Chemicals used for syntheses were commercially available. Solvents for spectral titrations were redistilled CH_3CN and deionized water.

Absorption and fluorescence spectra were recorded on Varian Cary 300 spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. Solutions were measured in a 1 cm quartz cell. Fluorescence quantum yields were measured using quinine sulfate as a standard (0.546 in 0.5 M H_2SO_4). ^{1}H NMR and ^{13}C NMR were acquired on Bruker AV400 and Varian Unity$^+$ 500 MHz NMR spectrometers. HRMS were obtained on a Micromass LCT spectrometer using methanol as the solvent. EPR experiments were carried out on a Bruker EMX-10/12 spectrometer.

All spectral titrations were carried out by keeping the sensor concentration constant while varying the metal ion concentration. Metal ions were used as their perchlorates. In the pH titration experiments, the solution pH was adjusted by dilute NaOH and HCl solutions that contained the same concentration of metal ion. Potassium chloride was employed to maintain solution ionic strength.

Preparation and characterization of 2–12 and 13.

2–12 were facilely synthesized from equimolar amounts of *N*-(substituted-benzoyl)hydrazine (2 mmol) with aldehyde or ketone (2 mmol) by a one-step reaction in ethanol, respectively. The mixture were refluxed for 3 h and then cooled down to room temperature. The crude products were isolated by filtration, and then recrystallized from absolute ethanol. New compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, and HRMS.

13 was synthesized from **3** (2 mmol) with 5 equivalents of $Cu(ClO_4)_2$ (10 mmol) in CH_3CN that were refluxed with stirring for 24 h, and then evaporated in vacuo. Aqueous ethylenediamine (1.0 mol L^{-1} × 25 mL) solution was added and the solution was then extracted by ethyl acetate (3 × 20 mL). The combined organic layer was thoroughly washed with water (3 × 20 ml), dried over anhydrous Na_2SO_4, and then concentrated under vacuum, then purified by column chromatography on silica gel with ethyl acetate-petroleum ether (1:5) as eluent. **13** was fully characterized by ^{1}H NMR, ^{13}C NMR, and HRMS to confirm the occurrence of oxidative cyclization reaction.

***N′*-(2-Methoxybenzylidene)-4-ethoxybenzohydrazide (2a).** ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 1.35 (t, 3H, *J* = 7.0 Hz), 3.87 (s, 3H), 4.09–4.13 (m, 2H), 7.02 (t, 3H, *J* = 8.0 Hz), 7.11 (d, 1H, *J* = 8.0 Hz), 7.41 (t, 1H, *J* = 7.5 Hz), 7.87 (d, 1H, *J* = 7.0 Hz), 7.92 (d, 2H, *J* = 8.5 Hz), 8.81 (s, 1H), 11.72 ppm (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ = 14.4, 55.6, 63.3, 111.7, 113.9, 120.6, 122.4, 125.2, 125.3, 129.4, 131.2, 142.4, 157.6, 161.1, 162.2 ppm; HRMS (ESI): m/z: calcd for $C_{17}H_{19}N_2O_3$: 299.1396 [M + H^+]; found: 299.1395 [M + H^+].

***N′*-(2-Methoxybenzylidene)-4-methylbenzohydrazide (2b).** ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 2.38 (s, 3H), 3.87 (s, 3H), 7.03 (t, 1H, *J* = 7.5 Hz), 7.11(d, 1H, *J* = 8.5 Hz), 7.33 (d, 2H, *J* = 8.0 Hz), 7.42 (t, 1H, *J* = 7.5 Hz), 7.85 (d, 2H, *J* = 8.0 Hz), 7.88 (d, 1H, *J* = 8.5 Hz), 8.82 (s, 1H), 11.78 ppm (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ = 20.9, 55.5, 111.7, 120.6, 122.4, 125.4, 127.5, 128.8, 130.4, 131.3, 141.6, 142.9, 157.6, 162.7 ppm; HRMS (ESI): m/z: calcd for $C_{16}H_{17}N_2O_2$: 269.1290 [M + H^+]; found 269.1295 [M + H^+].

***N′*-(2-Methoxybenzylidene)benzohydrazide (2c).** ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 3.87 (s, 3H), 7.04 (t, 1H, *J* = 7.5 Hz), 7.12 (d, 1H, *J* = 8.5 Hz), 7.43 (t, 1H, *J* = 7.5 Hz), 7.52 (t, 2H, *J* = 7.5 Hz), 7.59 (t, 1H, *J* = 7.0 Hz), 7.88 (d, 1H, *J* = 7.5 Hz), 7.93 (d, 2H, *J* = 7.5 Hz), 8.82 (s, 1H), 11.85 ppm (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ = 55.5, 111.6, 120.6, 122.3, 125.4, 127.5, 128.3, 131.4, 131.5, 133.3, 143.2, 157.7, 162.9 ppm; HRMS (ESI): m/z: calcd for $C_{15}H_{15}N_2O_2$: 255.1134 [M + H^+]; found 255.1141 [M + H^+].

***N′*-(2-Methoxybenzylidene)-4-chlorobenzohydrazide (2d).** ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 3.87 (s, 3H), 7.03 (t, 1H, *J* = 7.5 Hz), 7.12 (d, 1H, *J* = 8.0 Hz), 7.43 (t, 1H, *J* = 7.5 Hz), 7.61 (d, 2H, *J* = 8.0 Hz), 7.88 (d, 1H, *J* = 8.5 Hz), 7.96 (d, 2H, *J* = 8.5 Hz), 8.81 (s, 1H), 11.90 ppm (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ = 55.5, 111.7, 120.6, 122.2, 125.4, 128.4, 129.4, 131.5, 132.0, 136.5, 143.5, 157.7, 161.8 ppm; HRMS (ESI): m/z: calcd for $C_{15}H_{14}ClN_2O_2$: 289.0744 [M + H^+]; found 289.0754 [M + H^+].

4-Ethoxy-*N′*-(furan-2-ylmethylene)benzohydrazide (3a). ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 1.35 (t, 3H, *J* = 7.0 Hz), 4.11 (m, 2H), 6.64 (m, 1H), 6.91 (d, 1H, *J* = 3.2 Hz), 7.04 (d, 2H, *J* = 8.8 Hz), 7.85 (s, 1H), 7.87 (d, 2H, *J* = 8.8 Hz), 8.33 (s, 1H), 11.66 ppm (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 14.4, 63.3, 112.1, 113.1, 114.0, 125.1, 129.4, 136.9, 145.0, 149.5, 161.2, 162.4 ppm; HRMS (ESI): m/z: calcd for $C_{14}H_{15}N_2O_3$: 259.1083 [M + H^+]; found 259.1077 [M + H^+].

***N′*-(Furan-2-ylmethylene)-4-methylbenzohydrazide (3b).** ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 2.38 (s, 3H), 6.64 (s, 1H), 6.92 (s, 1H), 7.33 (d, 2H, *J* = 7.6 Hz), 7.81 (d, 2H, *J* = 7.6 Hz), 7.85 (s, 1H), 8.34 (s, 1H), 11.73 ppm (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 20.9, 112.1, 113.3, 127.5, 128.9, 130.4, 137.2, 141.7, 145.0, 149.4, 162.8 ppm; HRMS (ESI): m/z: calcd for $C_{13}H_{13}N_2O_2$: 229.0977 [M + H^+]; found 229.0977 [M + H^+].

***N′*-(Furan-2-ylmethylene)benzohydrazide (3c).** ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 6.65 (s, 1H), 6.94 (s, 1H), 7.53 (t, 2H, *J* = 6.4 Hz), 7.60 (t, 1H, *J* = 6.8 Hz), 7.86 (s, 1H), 7.90 (d, 2H, *J* = 7.2 Hz), 8.35 (s, 1H), 11.80 ppm (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 112.1, 113.4, 127.5, 128.4, 131.7, 133.3, 137.5, 145.1, 149.4, 163.0 ppm; HRMS (ESI): m/z: calcd for $C_{12}H_{11}N_2O_2$: 215.0821 [M + H^+]; found 215.0819 [M + H^+].

4-Chloro-*N′*-(furan-2-ylmethylene)benzohydrazide (3d). ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 6.65 (m, 1H), 6.96 (d, 1H, *J* = 3.2 Hz), 7.62 (d, 2H, *J* = 8.4 Hz), 7.87 (s, 1H), 7.93 (d, 2H, *J* = 8.4 Hz), 8.34 (s, 1H), 11.86 ppm (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 112.1, 113.7, 128.5, 129.4, 132.0, 136.5, 137.7, 145.2, 149.3, 161.9 ppm; HRMS (ESI): m/z: calcd for $C_{12}H_{10}ClN_2O_2$: 249.0431 [M + H^+]; found 249.0427 [M + H^+].

4-Ethoxy-*N′*-(1-(furan-2-yl)ethylidene)benzohydrazide (4). ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 1.35 (t, 3H, *J* = 7.0 Hz), 2.28 (s, 3H), 4.11 (m, 2H), 6.61 (m, 1H), 6.95 (s, 1H), 7.02 (d, 2H, *J* = 8.8 Hz), 7.80 (s, 1H), 7.86 (d, 2H, *J* = 8.8 Hz), 10.52 ppm

(s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 13.7, 14.5, 63.3, 111.2, 111.8, 113.8, 125.7, 129.9, 144.5, 145.1, 148.2, 151.8, 161.1 ppm; HRMS (ESI): m/z: calcd for $C_{15}H_{17}N_2O_3$: 273.1239 [M + H$^+$]; found 273.1245 [M + H$^+$].

***N′*-(2-Ethoxybenzylidene)-4-ethoxybenzohydrazide (5).** ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 1.34–1.41 (m, 6H), 4.09–4.15 (m, 4H), 7.00 (d, 1H, *J* = 7.6 Hz), 7.03 (d, 2H, *J* = 8.8 Hz), 7.09 (d, 1H, *J* = 8.0 Hz), 7.39 (t, 1H, *J* = 7.6 Hz), 7.88 (d, 1H, *J* = 7.6 Hz), 7.91 (d, 2H, *J* = 8.8 Hz), 8.80 (s, 1H), 11.75 ppm (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 14.5, 14.6, 63.3, 63.7, 112.7, 114.0, 120.6, 122.6, 125.2, 125.4, 129.5, 131.3, 142.5, 157.0, 161.2, 162.4 ppm; HRMS (ESI): m/z: calcd for $C_{18}H_{21}N_2O_3$: 313.1552 [M + H$^+$]; found 313.1556 [M + H$^+$].

***N′*-(2-Propoxybenzylidene)-4-ethoxybenzohydrazide (6).** ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 1.05 (t, 3H, *J* = 7.2 Hz), 1.36 (t, 3H, *J* = 7.2 Hz), 1.79 (m, 2H), 4.02 (t, 2H, *J* = 6.4 Hz), 4.11 (m, 2H), 6.99 (d, 1H, *J* = 7.2 Hz), 7.04 (d, 2H, *J* = 8.8 Hz), 7.08 (d, 1H, *J* = 8.4 Hz), 7.38 (m, 1H), 7.87 (s, 1H), 7.91 (d, 2H, *J* = 8.8 Hz), 8.80 (s, 1H), 11.76 ppm (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 10.5, 14.4, 22.0, 63.3, 69.4, 112.6, 113.9, 120.5, 122.6,125.3, 125.4, 129.5, 131.2, 142.4, 157.1, 161.1, 162.4 ppm; HRMS (ESI): m/z: calcd for $C_{19}H_{23}N_2O_3$: 327.1709 [M + H$^+$]; found 327.1703 [M + H$^+$].

***N′*-(2-Isopropoxybenzylidene)-4-ethoxybenzohydrazide (7).** ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 1.32 (d, 6H, *J* = 6.0 Hz), 1.36 (t, 3H, *J* = 6.8 Hz), 4.11 (m, 2H), 4.70 (m, 1H), 7.00 (t, 1H, *J* = 7.2 Hz), 7.03 (d, 2H, *J* = 8.8 Hz), 7.12 (d, 1H, *J* = 8.0 Hz), 7.37 (t, 1H, *J* = 8.0 Hz), 7.87 (d, 1H, *J* = 8.0 Hz), 7.91 (d, 2H, *J* = 8.8 Hz), 8.76 (s, 1H), 11.72 ppm (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 14.4, 21.8, 63.3, 70.4, 113.9, 114.5, 120.6, 123.6, 125.3, 125.6, 129.5, 131.1, 142.8, 156.0, 161.1, 162.3 ppm; HRMS (ESI): m/z: calcd for $C_{19}H_{23}N_2O_3$: 327.1709 [M + H$^+$]; found 327.1705 [M + H$^+$].

4-Ethoxy-*N′*-(thiophen-2-ylmethylene)benzohydrazide (8). ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 1.35 (t, 3H, *J* = 6.8 Hz), 4.11 (m, 2H), 7.04 (d, 2H, *J* = 8.8 Hz), 7.14 (m, 1H), 7.45 (d, 1H, *J* = 3.2 Hz), 7.66 (d, 1H, *J* = 4.8 Hz), 7.88 (d, 2H, *J* = 8.8 Hz), 8.67 (s, 1H), 11.68 ppm (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 14.4, 63.3, 114.0, 125.1, 127.7, 128.6, 129.4, 130.5, 139.2, 142.2, 161.2, 162.3 ppm; HRMS (ESI): m/z: calcd for $C_{14}H_{15}N_2O_2S$: 275.0854 [M + H$^+$]; found 275.0855 [M + H$^+$].

***N′*-Benzylidene-4-ethoxybenzohydrazide (9).** ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 1.36 (t, 3H, *J* = 7.0 Hz), 4.09–4.14 (m, 2H), 7.05 (d, 2H, *J* = 8.8 Hz), 7.43–7.48 (m, 3H), 7.73 (d, 2H, *J* = 6.4 Hz), 7.91 (d, 2H, *J* = 8.8 Hz), 8.45 (s, 1H), 11.73 ppm (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 14.4, 63.3, 114.0, 125.2, 126.9, 128.7, 129.5, 129.8, 134.4, 147.0, 161.2, 162.5 ppm; HRMS (ESI): m/z: calcd for $C_{16}H_{17}N_2O_2$: 269.1290 [M + H$^+$]; found 269.1289 [M + H$^+$].

4-Ethoxy-*N′*-(2-methylpropylidene)benzohydrazide (10). ^{1}H NMR (400 MHz, CD_3CN): δ = 1.10 (d, 6H, *J* = 6.8 Hz), 1.38 (t, 3H, *J* = 7.0 Hz), 2.51–2.59 (m, 1H), 4.07–4.12 (m, 2H), 6.96 (d, 2H, *J* = 7.2 Hz), 7.51 (s, 1H), 7.77 (d, 2H, *J* = 8.4 Hz), 9.67 ppm (s, 1H); ^{13}C NMR (400 MHz, DMSO-d_6, TMS): δ = 14.4, 19.6, 31.0, 63.2, 113.9, 125.4, 129.3, 155.9, 161.0, 162.2 ppm; HRMS (ESI): m/z: calcd for $C_{13}H_{19}N_2O_2$: 235.1447 [M + H$^+$]; found 235.1446 [M + H$^+$].

4-Phenyl-*N′*-(2-methoxybenzylidene)benzohydrazide (11). ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 3.88 (s, 3H), 7.05 (t, 1H, *J* = 7.6 Hz), 7.13 (d, 1H, *J* = 8.4 Hz), 7.43 (m, 2H), 7.52 (t, 2H, *J* = 7.6 Hz), 7.76 (d, 2H, *J* = 7.6 Hz), 7.84 (d, 2H, *J* = 8.4 Hz), 7.91 (d, 1H, *J* = 6.8 Hz), 8.05 (d, 2H, *J* = 8.4 Hz), 8.86 (s, 1H), 11.92 ppm (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 55.6, 111.8, 120.7, 122.3, 125.4, 126.6, 126.8, 128.1, 128.2, 129.0, 131.5, 132.0, 139.0, 143.1, 157.7, 162.5 ppm; HRMS (ESI): m/z: calcd for $C_{21}H_{19}N_2O_2$: 331.1447 [M + H$^+$]; found 331.1451 [M + H$^+$].

***N′*-(2-Methoxybenzylidene)-2-naphthohydrazide (12).** ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 3.89 (s, 3H), 7.06 (t, 1H, *J* = 7.2 Hz), 7.13 (d, 1H, *J* = 8.4 Hz), 7.45 (t, 1H, *J* = 7.6 Hz), 7.64 (m, 2H), 7.92 (d, 1H, *J* = 7.6 Hz), 8.01–8.09 (m, 4H), 8.58 (s, 1H), 8.88 (s, 1H), 12.03 ppm (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 55.6, 111.8, 120.7, 122.3, 124.2, 125.4, 126.8, 127.6, 127.8, 127.9, 128.0, 128.3, 130.6, 131.5, 132.0, 134.2, 143.1, 157.7, 162.8 ppm; HRMS (ESI): m/z: calcd for $C_{19}H_{17}N_2O_2$: 305.1290 [M + H$^+$]; found 305.1281 [M + H$^+$].

2-(4-Ethoxyphenyl)-5-furan-2-yl-1,3,4-oxadiazole (13a). ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 1.37 (t, 3H, *J* = 7.0 Hz), 4.14 (m, 2H), 6.83 (m, 1H), 7.16 (d, 2H, *J* = 8.8 Hz), 7.43 (d, 1H, *J* = 3.6 Hz), 8.00 (d, 2H, *J* = 8.8 Hz), 8.08 ppm (d, 1H, *J* = 1.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ = 14.4, 63.5, 112.6, 114.4, 115.1, 115.2, 128.5, 138.6, 146.8, 156.4, 161.4, 163.1 ppm; HRMS (ESI): m/z: calcd for $C_{14}H_{13}N_2O_3$: 257.0926 [M + H$^+$]; found 257.0927 [M + H$^+$].

2-Furan-2-yl-5-*p*-tolyl-1,3,4-oxadiazole (13b). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.44 (s, 3H), 6.62 (m, 1H), 7.23 (d, 1H, *J* = 3.2 Hz), 7.33 (d, 2H, *J* = 8.0 Hz), 7.67 (d, 1H, *J* = 1.2 Hz), 8.01 ppm (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.7, 112.2, 113.9, 120.8, 127.0, 129.8, 139.6, 142.5, 145.6, 157.4, 164.2 ppm; HRMS (ESI): m/z: calcd for $C_{13}H_{11}N_2O_2$: 227.0821 [M + H$^+$]; found 227.0822 [M + H$^+$].

2-Furan-2-yl-5-phenyl-1,3,4-oxadiazole (13c). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 6.63 (m, 1H), 7.24 (d, 1H, *J* = 3.6 Hz), 7.52 (s, 1H), 7.54 (m, 2H), 7.67 (d, 1H, *J* = 1.2 Hz), 8.13 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 112.2, 114.0, 123.5, 127.0, 129.0, 131.8, 139.4, 145.7, 157.4, 163.9 ppm; HRMS (ESI): m/z: calcd for $C_{12}H_9N_2O_2$: 213.0664 [M + H$^+$]; found 213.0669 [M + H$^+$].

2-(4-Chlorophenyl)-5-furan-2-yl-1,3,4-oxadiazole (13d). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 6.63 (m, 1H), 7.25 (d, 1H, *J* = 3.6 Hz), 7.51(d, 2H, *J* = 8.8 Hz), 7.68 (t, 1H, *J* = 0.8 Hz), 8.06 ppm (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 112.2, 114.3, 122.0, 128.2, 129.5, 138.1, 139.3, 145.8, 157.5, 163.1 ppm; HRMS (ESI): m/z: calcd for $C_{12}H_8ClN_2O_2$: 247.0274 [M + H$^+$]; found 247.0272 [M + H$^+$].

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