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N-[2-(4-Methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide: a receptor for acid binding

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Different hydrates of the receptor, *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide (**I**), and its co-crystals with acetic acid and L(+)α-hydroxy-phenylacetic acid are synthesised and their structures are studied. The acids such as acetic acid, L(+)α-hydroxy-phenylacetic acid quench fluorescence of **I**. The receptor **I** shows a fluorescence quenching on interaction with perchloric acid in benzene, whereas in methanol the solution of **I** results in the generation of a new fluorescence emission at higher wavelengths. The crystal structure of the perchlorate salt is determined to explain the protonation behaviour of the receptor **I** and the perchlorate salt in methanol leads to fluorescence emission at a place different from that of the parent compound.

Keywords: amide receptor; acid binding; fluorescence quenching; 8-hydroxyquinoline derivative; psuedo-polymorph

Introduction

Host–guest chemistry of molecules having fluorescence properties is important for the design of sensors (*1*) and also in material chemistry (*2*). The binding ability and performance of receptors for selective purpose needs careful attention (*3*). The compatibility of a receptor depends on the functional groups (*4*). Moreover, in solution they may have different speciations[11] and identification of each form becomes difficult. However, one of the ways to understand the properties of different forms that may exist in solution is by screening different species with different guests (*5*). Recently, we have shown that amide derivatives of 8-hydroxyquinoline compounds serve as templates for guest binding and have interesting fluorescence properties (*6*). The quinoline derivatives are acid-sensitive and the understanding of the binding ability with the guest molecule is of special interest (*7*). In this article, we have taken *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide (**I**) as an example of amide containing receptor for understanding its acid binding ability.

Result and discussions

N-[2-(4-Methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide was prepared by the reactions shown in Scheme 1. The anhydrous, monohydrate or dihydrate of *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide can easily be prepared by varying the solvent from which they are crystallised. Each of these forms, namely, anhydrous, monohydrate and dihydrate can be distinguished by solid-state IR spectra (refer to Supplementary Material). The anhydrous form has a sharp N–H absorption at 3328 cm^{-1}; this absorption occurs at 3572 and 3545 cm^{-1} in the monohydrate and dehydrate, respectively. The three co-crystals cannot be distinguished by comparing the ^{1}H NMR spectra in solution or by the fluorescence emission in solution.

The monohydrate and dihydrate of *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide (**I**) were prepared by crystallising **I** from ethylacetate or methanol/water as solvent, respectively. The crystal structures of the compound in anhydrous form (*6*) and as monohydrate and dihydrate are determined. Each of their crystal structure along with H-bond interactions is shown in Figure 1. In the anhydrous form, the molecules are arranged in parallel to each other to have a sheet-like structure; the sheet-like structures are formed through the N–H···O interactions [d_{D-A}, 2.904(3) Å; < D–H···A, 140.98°). On the other hand, the monohydrate forms a self-assembled dimeric structure which has water molecules occupying the concave structure formed due to the orientation of the amide groups with respect to the quinoline ring, as illustrated in Figure 1b. These monohydrate assemblies interact in a head-to-tail fashion with each other through hydrogen bonding so as to form a dimeric capsule-like structure. In this arrangement, the oxygen atom of the methoxy group forms a hydrogen bond with the water molecule (Figure 1b). The O4–H···N2 [d_{D-A}, 2.762(2) Å; < D–H···A, 174.07(2)°], N1–H···O4 [d_{D-A}, 2.932(2) Å; < D–H···A,

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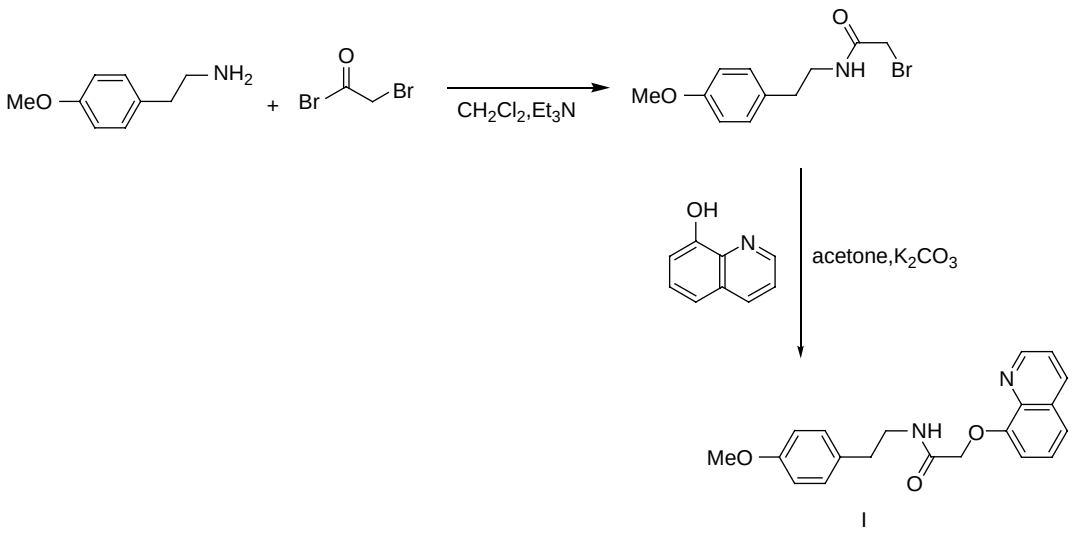

Scheme 1. Synthesis of *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide.

162.30(16)°] and O4–H···O1 [d_{D-A}, 3.007(19) Å; < D–H···A, 166.22(2)°] hydrogen-bond interactions are responsible for the stabilisation of dimeric structure. However, the dihydrate has an extended hydrogen-bonded structure. The extended structure in the dihydrate is formed by the interaction of monomeric half-capsules (similar to the monohydrate) with an additional intervening water molecule. The half-capsules are intervened by one water molecule each and the water molecules also form a hydrogen bond with the methoxy groups attached to the aromatic ring. This interaction leads to a zig–zag extended hydrogen-bonding network. The hydrogen bonds involved in the extended structure are O4–H···O5 [d_{D-A}, 2.907(5); < D–H···A, 168.0(4)], O3–H···O4 [d_{D-A}, 2.820(5); < D–H···A, 176.68(4)], N1–H···O3 [d_{D-A}, 2.946(5); < D–H···A, 153.33(3)] and O3–H···N2 [d_{D-A}, 2.809(5); < D–H···A, 171.73(8)], O4–H···O3 [d_{D-A}, 2.793(5); < D–H···A, 163.64(7)].

The ability to form different pseudo-polymorphs by **I** suggested that the molecule would interact with varieties of molecules to form co-crystals which are held by hydrogen bonds. Accordingly, the 1:1 co-crystals of *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide with acetic acid and L(+)α-hydroxy-phenylacetic acid was prepared. It formed a 1:2 co-crystal with acetic acid and a 1:1 co-crystal with L(+)α-hydroxy-phenylacetic acid. The structures of the co-crystals determined by X-ray crystallography are shown in Figure 2. In these co-crystals, the O–H groups of carboxylic acid are hydrogen bonded to the host molecule. In the case of co-crystal with acetic acid one of the OH groups of one acetic acid forms a cyclic structure by hydrogen bonds between the oxygen atoms, attached the ring and the amide N–H, whereas the amide carbonyl is held by the OH group of another acetic acid (Figure 2a). The hydrogen bonds that make the co-crystals of **I** with acetic acid are N1–H···O4 [d_{D-A}, 2.947(3) Å; < D-H···A, 158.48(3)°), O4–H···N2 [d_{D-A}, 2.665(3) Å; < D–H···A, 170.87(3)°] and O6–H···O1 [d_{D-A}, 2.591(3) Å; < D–H···A, 161.22(5)°).

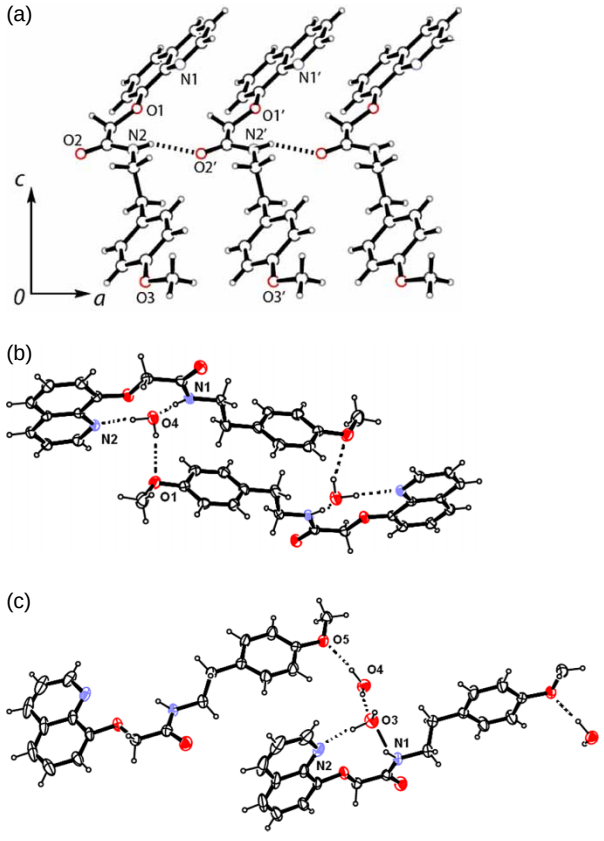

Figure 1. Hydrogen-bond interactions in (a) anhydrous, (b) monohydrate, (c) dihydrate of *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide.

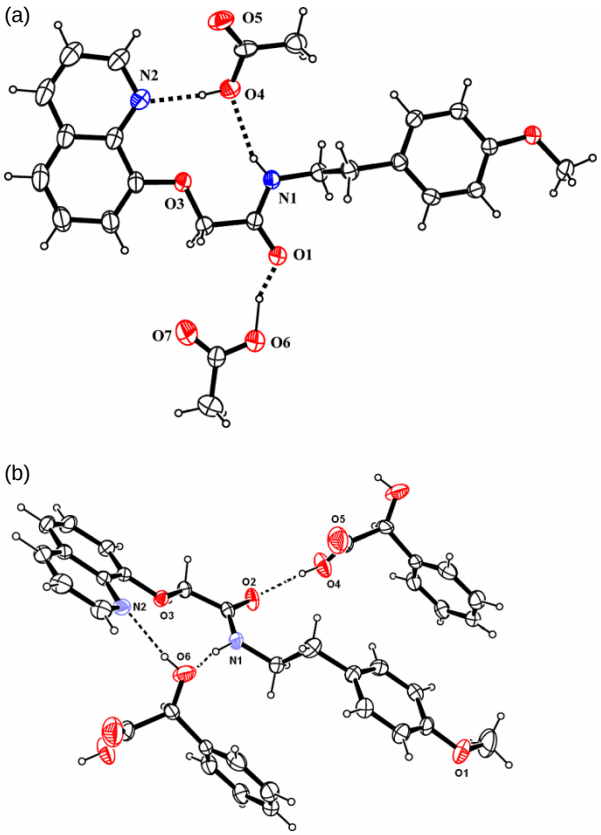

Figure 2. Structure of the co-crystal of **I** with (a) acetic acid and (b) L(+)α-hydroxy-phenylacetic acid.

The oxygen atom of the ethereal bond does not participate in the hydrogen bonding. On the other hand, the hydroxy-carboxylic acid forms an extended chain structure by bridging **I** through hydrogen bond between the OH group and the OH of the carboxylic acid group. The hydrogen bonds contributing to the bridging structure are O4–H···O2 [d_{D-A}, 2.615(11) Å; < D–H···A, 158.45°], O6–H···N2 [d_{D-A}, 2.738(11) Å; < D–H···A, 137.78°] and N1–H···O6 [d_{D-A}, 2.914(9) Å; < D–H···A, 150.61(7)°], respectively. These results clearly show that the packing patterns are different in each case and these patterns of **I** are decided by the guest molecules. Therefore, the physical properties of the co-crystals should be affected by the nature of guest molecules.

The ^{1}H NMR spectra of the compound in benzene-d^6 and methanol-d^4 (Figure 3a and c) showed that the aromatic region in the spectrum recorded in deuterated methanol is well resolved; whereas in the case of benzene-d^6 as solvent, it is less resolved. The intermolecular self association is possible in the case of the compound in benzene which probably makes the aromatic region of the spectra less resolved. The NH signal appearing at 8.6 ppm in deuterated benzene gets

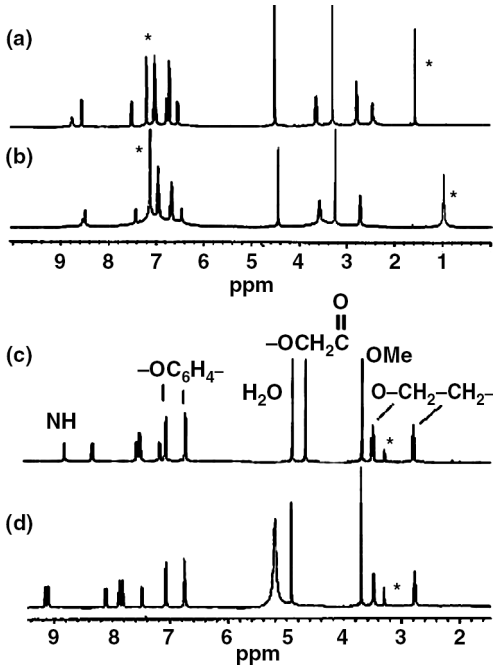

Figure 3. ^{1}H NMR spectra of **I** in (a) benzene-d^6, (b) benzene-d^6 with $HClO_4$, (c) CD_3OD, (d) CD_3OD with $HClO_4$. The solvent peaks are marked as ∗.

shifted to 8.8 ppm in deuterated methanol, suggesting its participation in intermolecular hydrogen bond. The effect is reflected in the fluorescence emission of the compound. The compound on excitation at 310 nm shows emission at 383 nm ($\varphi = 0.36$) in benzene, whereas it shows an emission at 395 nm ($\varphi = 0.07$) in methanol. There is an intensity difference in the emission, the compound in benzene emits with approximately six times higher intensity than methanol. This is attributed to the formation of intermolecular hydrogen bond in a protic solvent, which affects the fluorescence emission. In the absence of intramolecular H-bonding the 8-hydroxyquinoline itself has solvent-dependent fluorescence properties (*6*).

The study of chiral recognition by fluorescence probe is a very important issue (*3*). Since, we could prepare the co-crystal of α-hydroxy-phenylacetic acid, we investigated the effect of the addition of the two optical isomers of α-hydroxy-phenylacetic acid to a solution of **I** in benzene. It is observed that in methanol the emission at 395 nm gets quenched on the addition of either of the optical isomers. The trend in the relative decrease in intensity with an increase in the concentration of either of the isomers has a very small difference, which may be neglected within the experimental error. This suggests that the binding constant of the two optical isomers of α-hydroxy-phenylacetic acid with **I** as host are comparable and the two bound isomers to **I** and cannot be differentiated by simple fluorescence emission intensity. The binding constants of the two

Table 1. Binding constant of **I** at 27°C with different guest molecules

	D(−)Mandelic acid	L(+)Mandelic acid	Acetic acid	$HClO_4$ (in methanol)	$HClO_4$ (in benzene)
Binding constant (M^{-1})	6.85×10^5	4.25×10^5	3.33×10^5	9.15×10^5	6.84×10^7

isomers were determined and are listed in Table 1 and the values support the comparable values for the two optical isomers.

The effect of hydrogen bonding in the fluorescence emission of **I** was studied by adding acetic acid to a benzene solution of **I**. Fluorescence quenching of **I** took place on the addition of acetic acid. This result is also in agreement with the observation of a strong hydrogen bonding in the crystal structure of co-crystal of **I** with acetic acid. In an earlier study, the two optical isomers of α-hydroxy-phenylacetic acid were detected by fluorescence of chiral host–guest complex (*8*) but in our case the host does not have chiral centre, hence no distinction could be made.

It has been observed that fluorescence quenching occurs when a solution of **I** is treated with perchloric acid in benzene (Figure 4a). Whereas, when a methanolic solution of **I** is treated with perchloric acid, fluorescence quenching is observed at 395 nm, but a new fluorescence emission state is generated at 493 nm. This process passes through an isoemissive point, suggesting a direct conversion of one species to another. The observation is attributed to the protonation of ring nitrogen in methanol. It is clear that the protonated and the hydrogen-bonded states of **I** are distinguishable. The process may be attributed to the fact that benzene being an aprotic solvent allows the formation of an ion-pair whereas in the case of methanol the proton transfer takes place leading to a new state. Further support to this statement comes from the fact that the ^{1}H NMR spectra of compound **I** in methanol-d^4 with perchloric acid and **I** in benzene-d^6 with perchloric acid are different (Figure 3b and d), confirming the two different states in two different solvents. In benzene, perchloric acid ionises less relative to methanol; therefore, in benzene perchloric acid is involved in hydrogen bonding without protonating compound **I**. But in the protic solvent methanol, the protonation of the ring nitrogen leads to a new state; this also significantly affects the chemical shifts of the ring protons. In the former case, the amide N–H peak at 8.8 ppm is shifted towards lower ^{1}H NMR chemical shift recorded in two different solvents. The perchlorate salt could be isolated as a tetrahydrate. The fluorescence emission of 8-hydroxyquinoline is independent of the solvent nature as the intramolecular hydrogen bonding predominates; however, due to a competition between intra- and inter-molecular hydrogen bonding at low temperature quenching takes place by H-bond formation with the solvent (*7*b). In our system, the OH in the ring is not available to make assembly of the isoquioline part of the molecule, thus, it behave in a trend of 5-hydroxyquinoline, which shows a solvent-dependent fluorescence emission (*7*b). We have determined the binding constant of perchloric acid in benzene and methanol and they are found to be largely different (Table 1). These two values cannot be directly compared because in the case of methanol it corresponds to the proton exchange process whereas in the case of benzene it is an ion-pair formation leading to only quenching of fluorescence. To have the structural aspect of the protonated species, we determined the crystal structure of the perchlorate salt of **I**. The structure of the salt is shown in Figure 5. The salt was obtained in the hydrated form having four H-bonded water molecules in the crystal lattice. In this salt, the protonated N-atom of the

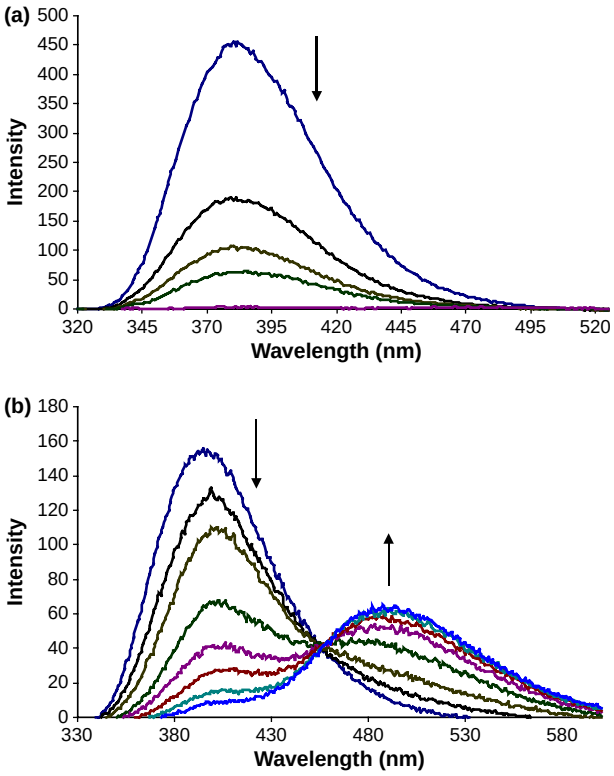

Figure 4. Fluorescence emission (λ_{ex} 310 nm) of amide **I** in (a) benzene (3.3×10^{-5} M) on addition of $HClO_4$ solution (2×10^{-2} M; 5 μl in each aliquot) and (b) methanol (6.6×10^{-4} M) on addition of $HClO_4$ (10^{-1} M; 5 μl in each aliquot) solution in methanol.

quinoline ring forms H-bond with water molecules. The water molecules with the aid of these interactions form a hexameric ring system. There are two different types of hexameric water clusters that are present in the lattice, illustrated in Figure 5. One hexameric unit is encapsulated by two layers of the parent compound. The O4–H···O6 [d_{D-A}, 2.761(4) Å; < D–H···A, 166.85(3)°], O4–H···O7 [d_{D-A}, 2.69(4) Å; < D–H···A, 165.21(3)°] and O7–H···O6 (d_{D-A}, 2.79(4)Å, < D–H···A, 166.60(5)°] hydrogen-bonding interactions are responsible for the formation of this hexameric unit to form a capsule-like structure of the parent molecules with the encapsulated water molecules. The encapsulated water molecules are stabilised by intermolecular N1–H···O4 [d_{D-A}, 2.95(4) Å; < D–H···A, 161.83(3)°] and N2–H···O4 [d_{D-A}, 2.71(3) Å; < D–H···A, 159.60(2)°] interactions rather than the intermolecular O–H···O interactions between water molecules which are responsible for the formation of hexameric H-bonded water cluster. The perchlorate anions are held in a lattice through O8–H···O7 [d_{D-A}, 2.98(4) Å; < D–H···A, 168.88°] and O5–H···O8 [d_{D-A}, 3.21(5) Å; < D–H···A, 156.73(4)°] H-bonding interactions with water molecules. Besides, weak C–H···O interactions [C13–H···O11 [d_{D-A}, 3.45(4) Å; < D–H···A, 158.23 °) and C17–H···O9 (d_{D-A}, 3.38(4) Å, < D–H···A, 167.20 °)] are also present between the hydrogen atom at C13 of the quinoline ring and the oxygen atom of the prechlorate anion. The encapsulated dimeric units are assembled through a hexameric hydrogen-bonded network, where the carbonyl groups of amides participate in intermolecular hydrogen bonding with water molecules through O5–H···O2 [d_{D-A}, 2.81(4) Å; < D–H···A, 173.26(3)°] and O6–H···O2 [d_{D-A}, 2.84(4) Å; < D–H···A, 158.24(3)°] interactions. The water molecules are assembled via the O6–H···O5 [d_{D-A}, 2.68(4) Å; < D–H···A, 165.65(4)°] hydrogen-bonded interaction so that the capsule-like structures are held together. The solid-state FT-IR spectra of the salt has a strong absorption peak at 1668 cm^{-1}, due to the C=O group of amide. There is also a strong absorption peak at 1114 cm^{-1} due to the perchlorate group. The perchlorate salt has fluorescence emission at 395 nm suggesting that the emission that occurs at this wavelength in a methanolic solution of **I** with perchloric acid corresponds to the formation of the N-protonated perchlorate salt.

In conclusion, we have synthesised and characterised various co-crystals/hydrates of *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide. The isolation of the co-crystal of L(+)α-hydroxy-phenylacetic acid with *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide reflects the binding ability of a chiral hydroxy acid with the host **I**. Finally, a clear distinction by fluorescence spectroscopy on hydrogen-bonding interaction with the receptor **I** by an acid and formation of a protonated receptor **I** is established.

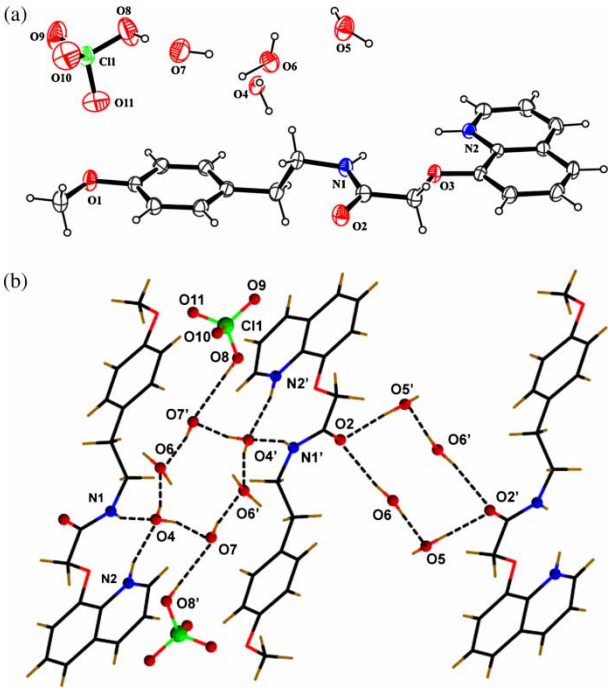

Figure 5. (a) Crystal structure of perchlorate salt of **I** and (b) different water clusters helping in formation of self-assembly of the perchlorate salt of **I**.

Experimental section

All the solvents used in this study were of spectroscopic grade. The fluorescence spectra were recorded on a Carry Fluorimeter by exciting at an appropriate wavelength. Fluorescence titrations were done by taking the appropriate amount of sample in a quartz cell and adding the appropriate amount to the solution using a micropipette. The UV–visible spectra were recorded using a Perkin-Elmer Lamda spectrophotometer by taking the appropriate solution in a quartz cell. The quantum yields were determined by comparing the corrected area in visible absorption and fluorescence emission with anthracene as the standard.

X-ray crystallography

X-ray crystallographic data were collected at 296 K with Mo K_α radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-square calculations using SHELXTL software. All the

non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The H-atoms, except those attached to N and O, were placed at their calculated positions and refined in the isotropic approximation; those attached to heteroatoms (N and O) were located in the difference Fourier maps and refined with isotropic displacement coefficients. The crystallographic parameters for the structures determined are given in Table 2.

Synthetic procedures

N-[2-(4-Methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide was prepared by reacting 2-bromo-*N*-[2-(4-methoxy-phenyl)-ethyl] acetamide with 8-hydroxyquinoline. 2-Bromo-*N*-[2-(4-methoxy-phenyl)-ethyl] acetamide was prepared by the following procedure: 2-(4-methoxyphenyl)ethylamine (1.51 g, 10 mmol) was dissolved in dry dichloromethane (20 ml) and triethylamine (1.01 g, 10 mmol) was added to this solution. The solution was stirred at 0°C for 10 min after which bromoacetyl bromide (2.42 g, 12 mmol) was added dropwise to the stirred solution over a period of 30 min. The reaction mixture was then stirred overnight. Subsequently, the reaction mixture was filtered to remove the hydrobromide salts, and the filtrate collected. The filtrate was washed with water (10 ml), dried over anhydrous sodium sulphate and then the solvent was removed under reduced pressure. 2-Bromo-*N*-[2-(4-methoxy-phenyl)-ethyl] acetamide was obtained as a brown solid. The crude product thus obtained was recrystallised from dichloromethane.

2-Bromo-*N*-[2-(4-methoxy-phenyl)-ethyl] acetamide (2.72 g, 10 mmol), 8-hydroxyquinoline (1.45 g, 10 mmol) and K_2CO_3 (2.07 g, 15 mmol) were dissolved in dry acetone (20 ml) under nitrogen atmosphere and the reaction mixture was stirred at 60 °C for 10 h. (The progress of the reaction was monitored at regular intervals using TLC). After completion of the reaction the solvent was removed under reduced pressure. On removal of the solvent, a brown solid was obtained. The solid was washed with dilute sodium hydroxide solution (5 ml, 5% aqueous), and water (5 ml) and then extracted with dichloromethane. The organic extracts were collected over anhydrous sodium sulphate. Subsequent removal of the solvent gave the crude product, which was purified by chromatography (silica gel; hexane/ethyl acetate, 3:2). Isolated yield, 46%.

The monohydrate of **I** was obtained by dissolving **I** in ethylacetate and allowing the solution to crystallise. After 3 days, block-like crystals appeared. The crystals were collected and dried in air.

The spectroscopic data for monohydrate of **I**: ^{1}H NMR ($CDCl_3$): 8.80 (1*H*, dd, $J = 4.4$, 1.6 Hz), 8.34 (1*H*, s), 8.19 (1*H*, dd, $J = 8.4$, 1.6 Hz), 7.48 (3*H*, m), 7.12 (1*H*, dd, $J = 6.4$, 2.4 Hz), 7.01 (2*H*, d, $J = 8.8$ Hz), 6.67 (2*H*, d, $J = 8.8$ Hz), 4.76 (2*H*, s), 3.73 (3*H*, s), 3.57 (2*H*, q, $J = 13.2$ Hz), 2.89 (2*H*, s), 2.78 (2*H*, t, $J = 7.2$ Hz). ^{13}C NMR ($CDCl_3$): 168.59, 158.2, 153.77, 149.29, 136.6, 131.1, 129.73, 127.0, 122.05, 121.5, 113.93, 111.59, 69.60, 55.27, 40.73, 34.79. IR (KBr, cm^{-1}): 3572(s), 3254(bs), 3053(bs), 2956(m), 2932(m), 2874(m), 1657 (amide C═O), 1611(m), 1540(m), 1506(s), 1449(s), 1375(s), 1320(s),1302(m), 1254(s), 1238(s), 1180(s), 1111(s), 1025(s), 826(s), 798(s), 750(s), 600(s), 553(m), 517(m).

Dihydrate of compound I

The amide **I** was dissolved in methanol:water (1:1), and kept for crystallisation. After 10 days, needle-like crystals appeared. The crystals were collected and dried in air. IR (KBr, cm^{-1}): 3545(s), 3350(bs), 2932(m), 1666 (amide C═O stretch), 1612(m), 1547(s), 1511(s), 1473(m), 1380(m), 1320(m), 1298(m), 1258(s), 1241(s), 1175(m), 1111(s), 1020(m), 822(m), 788(m), 761(m), 747(m), 588(w), 521(w), 487(m).

Preparation of perchlorate salt of **N-***[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide (I)*

N-[2-(4-Methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide (0.1 g) was taken in a round-bottom flask. To this, water (3 ml) and $HClO_4$ (60%, 40 μl) were added. The solution was warmed for 5–10 min until all amide **I** was dissolved. The resultant solution was kept for crystallisation. After 15 days, needle-like yellow crystals appeared. ^{1}H NMR (D_2O): 9.12 (1*H*, d, $J = 8.8$ Hz), 9.0 (1*H*, d, $J = 2.4$ Hz), 8.08 (1*H*, dd, $J = 8.4$, 5.2 Hz), 7.89 (1*H*, d, $J = 8.4$ Hz), 7.77 (1*H*, t, $J = 8$ Hz), 7.29 (1*H*, d, $J = 8$ Hz), 7.02 (2*H*, d, $J = 8.4$ Hz), 6.66 (2*H*, d, $J = 8.4$ Hz), 4.88 (2*H*, s), 3.69 (3*H*, s), 3.55 (2*H*, t, $J = 6.4$ Hz), 2.75 (2*H*, t, $J = 6.4$ Hz). IR (KBr, cm^{-1}): 3296(bs), 3093(bs), 2935(m), 1668 (amide C═O stretch), 1600(s), 1550(s), 1546(s), 1512(s), 1440(m), 1392(m), 1299(s), 1244(s), 1179(m),1144(s) 1114(s), 1083(s), 881(m), 749(s), 636(s), 625(s) 564(w), 524(w), 487(m).

Preparation of co-crystals of **N-***[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide (I) with acetic acid*

Amide **I** (0.1 g), acetic acid (25 μl) and water (3 ml) were mixed in a round-bottom flask. The mixture was warmed for 5–10 min; a homogeneous solution was obtained. The resultant solution was kept for crystallisation. After 20 days, colourless crystals appeared. ^{1}H NMR (D_2O): 9.07 (1*H*, d, $J = 8.8$ Hz), 8.98 (1*H*, d, $J = 2.4$ Hz), 8.04 (1*H*, t, $J = 5.2$ Hz), 7.86 (1*H*, d, $J = 8.4$ Hz), 7.75 (1*H*, t, $J = 8.4$ Hz), 7.27 (1*H*, d, $J = 7.6$ Hz), 7.0 (2*H*, d,

Table 2. Crystallographic parameters of co-crystals of **I**

	Monohydrate of **I**	Dihydrate of **I**	Co-crystal of **I** with acetic acid	Co-crystal of **I** with L(+) α-hydroxy-phenylacetic acid	Co-crystal of **I** with perchloric acid
Formula	$C_{20}H_{22}N_2O_4$	$C_{20}H_{24}N_2O_5$	$C_{24}H_{28}N_2O_7$	$C_{28}H_{28}N_2O_6$	$C_{20}H_{27}ClN_2O_{11}$
Mol. wt.	354.40	372.41	456.48	488.52	506.89
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	Cc	P-1	P-1	P-1
Temperature/K	296	296	296	296	296
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073
a/Å	7.1037(15)	21.9919(4)	5.06960(10)	9.3056(3)	8.3309(8)
b/Å	11.806(3)	4.80880(10)	9.0991(2)	9.6907(4)	9.2665(9)
c/Å	12.231(3)	20.9465(4)	26.4899(6)	16.2492(6)	16.4365(15)
α/°	62.431(6)	90.00	91.913(2)	77.184(2)	87.815(7)
β/°	87.595(7)	119.546(3)	91.993(2)	74.467(2)	76.962(7)
γ/°	88.176(6)	90.00	100.875(2)	64.461(2)	79.988(7)
V/Å^3	908.4(3)	1927.13(6)	1198.28(4)	1264.28(8)	1217.3(2)
Z	2	4	2	2	2
Density/Mgm^{-3}	1.296	1.284	1.265	1.283	1.388
Abs. coeff./mm^{-1}	0.091	0.093	0.093	0.091	0.217
Abs. correction	None	None	None	None	None
F(000)	376	792	484	516	536
Total no. of reflections	9706	8211	11,741	18,094	17,295
Reflections, $I > 2\sigma(I)$	4392	3569	5697	6032	5698
Max. 2θ/°	28.21	28.30	28.30	28.20	28.40
Ranges (*h*,*k*,*l*)	$-9 \Leftarrow h \Leftarrow 9$ $-15 \Leftarrow k \Leftarrow 15$ $-16 \Leftarrow l \Leftarrow 15$	$-26 \Leftarrow h \Leftarrow 28$ $-6 \Leftarrow k \Leftarrow 6$ $-27 \Leftarrow l \Leftarrow 24$	$-6 \Leftarrow h \Leftarrow 6$ $-12 \Leftarrow k \Leftarrow 12$ $-35 \Leftarrow l \Leftarrow 35$	$-12 \Leftarrow h \Leftarrow 12$ $-12 \Leftarrow k \Leftarrow 12$ $-20 \Leftarrow l \Leftarrow 21$	$-11 \Leftarrow h \Leftarrow 11$ $-12 \Leftarrow k \Leftarrow 11$ $-21 \Leftarrow l \Leftarrow 21$
Complete to 2θ (%)	97.8	97.9	95.5	96.7	93.2
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4392/0/248	3569/0/265	5697/0/313	6032/0/332	5698/0/345
Goof (F^2)	1.046	1.021	1.023	1.071	0.987
R indices [$I > 2\sigma(I)$]	0.0422	0.0469	0.0618	0.1613	0.0624
R indices (all data)	0.0594	0.0823	0.1396	0.1821	0.1375

$J = 6.4$ Hz), 6.65 (2*H*, d, $J = 8.8$ Hz), 4.89 (2*H*, s), 3.68 (3*H*, s), 3.53 (2*H*, t, $J = 5.2$ Hz), 2.74 (2*H*, t, $J = 5.2$ Hz), 2.18 (3*H*, s). IR (KBr, cm^{-1}): 3311(bs), 3054(m), 1655(s), 1613(m), 1556(m), 1513(s), 1476(m), 1436(m), 1380(m), 1320(m), 1268(m), 1251(s), 1187(m), 1178(m), 1117(s), 1086(m), 1027(m), 818(s), 793(m), 751(s), 599(w), 519(w),489(w).

Preparation of co-crystals of N-*[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide (I) with* L(+)α-*hydroxy-phenylacetic acid*

N-[2-(4-Methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)acetamide (**I**) (0.1 g, 0.3 mmol) and L(+)α-hydroxy-phenylacetic acid (0.05 gm, 0.3 mmol) were mixed and dissolved in ethylacetate (5 ml). The resultant solution was kept for crystallisation. After 4 days, colourless crystals appeared. ^{1}H NMR ($CDCl_3$): 8.93 (1*H*, s), 8.30 (1*H*, d, $J = 8.4$ Hz), 8.0 (1*H*, s), 7.53 (3*H*, m), 7.47 (2*H*, d, $J = 8.4$ Hz), 7.32 (3*H*, m), 7.10 (1*H*, d, $J = 5.6$ Hz), 6.97 (2*H*, d, $J = 8.4$ Hz), 6.65 (2*H*, d, $J = 8.4$ Hz), 5.17 (1*H*, s), 4.66 (2*H*, s), 3.73 (3*H*, s), 3.48 (2*H*, m), 2.71 (2*H*, t, $J = 7.2$ Hz), 2.17 (1*H*, s). IR (KBr, cm^{-1}): 3257(bs), 3063(bs), 3033(bs), 3007(bs), 2932(m), 2832(m), 1742(s), 1722(m), 1628(s), 1510(s), 1472(w), 1455(w), 1437(w), 1376(m), 1311(m), 1263(m), 1247(s), 1180(s), 1116(s), 1043(m), 823(m), 785(m), 749(m), 721(m), 701(m), 679(w), 616(w), 489(w).

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