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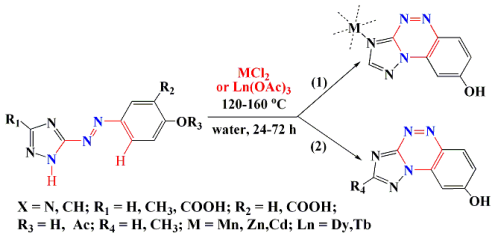
A novel approach for the direct construction of 1,2,4–triazine core via metal catalyzed intramolecular C–H/N–H functionalization has been developed.



X = N, CH; R_1 = H, CH_3, COOH; R_2 = H, COOH;
R_3 = H, Ac; R_4 = H, CH_3; M = Mn, Zn,Cd; Ln = Dy,Tb

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ARTICLE

M^{2+}, Ln^{3+}-Catalyzed Synthesis of [1,2,4]Triazine Core via Intramolecular C-H/N-H Functionalization and C-N Bond Formation (M = Mn, Zn, Cd; Ln = Dy, Tb)

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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A novel approach for the direct synthesis of the 1,2,4-triazine core starting from eight azo conjugated aromatic compounds of 5-azo-(1,2,4-triazolyl) salicylic acid, 5-azo-(3-methyl-1,2,4-triazolyl) salicylic acid, 5-azo-(3-carboxyl-1,2,4-triazolyl) salicylic acid, 5-azo-(1,2-pyrazolyl) salicylic acid, 4-azo-(1,2,4-triazolyl) phenol, 4-azo-(3-carboxyl-1,2,4-triazolyl) phenol, 4-azo-(1,2-pyrazolyl) phenol, 5-azo-(1,2,4-triazolyl) acetylsalicylic acid via transition or lanthanide metal catalyzed intramolecular C-H/N-H functionalization and C-N bond formation has been developed under one-step hydrothermal synthetic condition.

Introduction

Substituted 1,2,4-triazine derivatives have attracted intense interest due to their great importance as biological agents in medicinal and agricultural fields.[1] In the pursuit of various new medicinal agents containing a 1,2,4-triazine core, additional nitrogen-containing heterocyclic scaffolds such as pyrrole, imidazole and triazole, have been usually incorporated in the 1,2,4-triazine core via various synthetic methods.[1-3] Sadchikova and Partridge reported the synthesis of a substituted 1,2,4-triazine derivative of [1,2,4]triazolo[5,1-c][1,2,4] benzotriazine-8-ol (TBT) and pyrazolo[5,1-c][1,2,4]benzotriazine-8-ol (PBT) via the progress of intramolecular dealcoholization and dehydration reactions from azo based heterocyclic compounds, respectively.[3] Recently, the transition metal-catalyzed inter- and intramolecular C-H and N-H functionalization or activation and C-N bond formation for the direct synthesis of five-membered nitrogen containing heterocyclic ring derivatives (e.g., carbazole) have shown increasing popularity.[4,5] The C-H bond functionalization has shown widespread applications and industrial potential.[4,6] Two possible mechanisms of Heck-type and Wacker-type cyclization/(-hydride elimination) for construction of heterocyclic rings have been proposed when metal Pd serves as catalyst.[4b,7] On the other hand, activation of C-H bonds induced by lanthanide metal has been also developed and proven to be particularly effective.[8] However, the synthetic method via direct conversion of C-H to C-N bond to synthesize the six-membered nitrogen containing heterocyclic ring of 1,2,4-triazine core via transition metal or lanthanide metal-catalyzed cross-dehydrogenative coupling reaction, to the best of our knowledge, has not been reported although many synthetic methods for substituted 1,2,4-triazine derivatives have been well-documented.[1-3] Therefore, it is considered as a great challenge to synthesize 1,2,4-triazine core via the transition or lanthanide metal-catalyzed inter- and intramolecular C-H and N-H functionalization and C-N bond formation. Herein, we describe a new approach to the direct construction of the 1,2,4-triazine core starting from eight azo conjugated aromatic compounds via transition or lanthanide metal catalyzed cross-dehydrogenative coupling reactions under hydrothermal conditions. Six 1,2,4-triazine derivatives of a hydrated [1,2,4]triazolo[5,1-c][1,2,4]benzotriazine-8-ol (TBT) of $C_{32}H_{26}N_{20}O_7$ (**1**), three complexes of $[M(TBT)_2(H_2O)_4]\cdot 2H_2O$ (M = Mn (**2**), Zn(**3**), Cd(**4**), a hydrated 5-methyl-[1,2,4]triazolo[5,1-c][1,2,4]benzotriazine-8-ol (MTBT) of $C_{18}H_{16}N_{10}O_3$ (**5**) and another organic compound of pyrazolo[5,1-c][1,2,4]benzotriazine-8-ol (PBT) (**6**) were synthesized. In particular, the reaction conditions described herein significantly improved the efficiency and practicality of 1,2,4-triazine core formation via a transition or lanthanide metal catalyzed cross-dehydrogenative coupling reaction under one-step hydrothermal synthetic method. Most of target products with high yields are crystals and easy-to-handle and this synthetic protocol is thus simple and easily controlled.

Experimental

All the commercial reagents and solvents were used without further purification unless otherwise stated.

Quantum Calculations. All the quantum-chemical calculations were done with the Gaussian 09 suite. The calculations were performed using the time dependent density functional theory (TD-DFT) at B3LYP/6-31G* level based on the crystal structures for the solid samples obtained in this work.

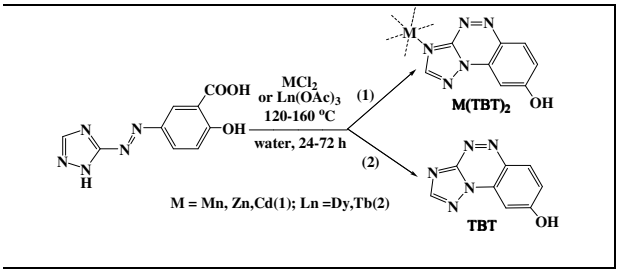
Compounds of eight azo conjugated aromatic compounds of 5-azo-(1,2,4-triazolyl) salicylic acid , 5-azo-(3-carboxyl-1,2,4-triazolyl) salicylic acid, 4-azo-(1,2,4-triazolyl) phenol, 4-azo-(3-carboxyl-1,2,4-triazolyl) phenol, 5-azo-(1,2,4-triazolyl) acetylsalicylic acid, 5-azo-(3-methyl-1,2,4-triazolyl) salicylic acid, 4-azo-(1,2-pyrazolyl) phenol and 5-azo-(1,2-pyrazolyl) salicylic acid were synthesized according to the literature procedures.[9,10]

5-azo-(1,2,4-triazolyl) salicylic acid. Yellow solid; 88% (4.101g, 0.0176mol) yields, based on 1.68g 0.02 mol 3-amino-1,2,4-triazole. Anal. Calcd. of $C_9H_{11}N_5O_5$ (%): C, 40.11; H, 4.08; N, 26.0. Found(%): C, 40.03; H, 4.32; N, 25.81. FT-IR (KBr, cm^{-1}): 3485s, 1628s, 1577m, 1434m, 1386m, 1297m, 1178m, 1076w, 877m, 839m, 555w. The ^1H NMR Spectrum and crystallographic data were reported in our previous literature.[10] **5-azo-(3-methyl-1,2,4-triazolyl) salicylic acid**. Yellow solid; 80% (3.952g, 0.016mol) yields, based on 1.96g 0.02 mol 3-methyl-5-amino-1,2,4-triazole. Anal. Calcd. of $C_{10}H_9N_5O_3$ (%): C, 48.58; H, 3.67; N, 28.33. Found(%): C, 48.43; H, 3.69; N, 28.31. FT-IR (KBr, cm^{-1}): 3537s, 3329m, 2800s, 1666s, 1588s, 1487s, 1366s, 1290s, 1226s, 1187s, 1061s, 942m, 890m, 836s, 770s, 693m, 659m, 560s, 513m. MS (ESI) m/z $[M-H]^-$ $C_{10}H_8N_5O_3^-$ requires 246.20, found 246.25. **5-azo-(3-carboxyl-1,2,4-triazolyl) salicylic acid**. Yellow solid; 83% (4.598g, 0.0166mol) yields, (based on 2.56g, 0.02 mol 3-carboxyl-5-amino-1,2,4-triazole). Anal. Calcd. of $C_{10}H_7N_5O_5$ (%): C, 43.33; H, 2.55; N, 25.27. Found(%): C, 43.39; H, 2.50; N, 25.31. FT-IR (KBr, cm^{-1}): 3113s, 2908s, 2808m, 1672s, 1587s, 1542m, 1485s, 1443s, 1345s, 1303m, 1262s, 1228s, 1200s, 980m, 840m, 801m, 758m, 675m, 560m. MS (ESI) m/z $[M-2H]^{2-}$ $C_{10}H_5N_5O_5^{2-}$ requires 137.56, found 137.18. ^1H NMR (400 MHz, DMSO) δ 8.33 (d, J = 2.5 Hz, 1H), 8.07 (dd, J = 8.9, 2.6 Hz, 1H), 7.14 (d, J = 8.9 Hz, 1H). **5-azo-(1,2-pyrazolyl) salicylic acid**. Brown yellow solid; 80% (3.008g, 0.016mol) yields, based on 1.66g, 0.02mol 3-aminopyrazole. Anal. Calcd. of $C_{10}H_8N_4O_3$ (%): C, 51.73; H, 3.47; N, 24.13. Found(%): C, 51.70; H, 3.49; N, 24.10. FT-IR (KBr, cm^{-1}): 3305s, 1667m, 1588s, 1484s, 1343s, 1259s, 1175s, 1098m, 1074m, 824m, 795m, 766m, 677m, 555m, 517m; ^1H NMR (400 MHz, DMSO) δ 13.30 (s, 1H), 10.25 (s, 1H), 7.83 (s, 1H), 7.75 (d, J=8.4 Hz, 2H), 6.93 (d, J=8.4 Hz, 2H), 6.48 (s, 1H), MS (ESI) m/z $[M-H]^-$ $C_{10}H_7N_4O_3^-$ requires 231.0, found 230.9; $[M+H]^+$ $C_{10}H_9N_4O_3^+$ requires 233.0, found 232.9. **4-azo-(1,2,4-triazolyl) phenol**. Yellow solid; 86% (3.251g, 0.0172 mol) yields, based on 1.68g 0.02 mol 3-amino-1,2,4-triazole. Anal. Calcd. of $C_8H_7N_5O$ (%): C, 50.79; H, 3.73; N, 37.02. Found(%): C, 50.70; H, 3.75; N, 36.99. FT-IR (KBr, cm^{-1}): 3348s, 3131s, 1671m, 1610m, 1590s, 1486s, 1486s, 1342m, 1266s, 1150s, 977m, 882m, 842s, 761m, 637m, 520m; ^1H NMR (400 MHz, DMSO) δ 14.51 (s, 1H), 10.47 (s, 1H), 8.69 (s, 1H), 7.84 (d, J=7.7 Hz, 2H), 6.97 (d, J=7.9 Hz, 2H); MS (ESI) m/z $[M-H]^-$ $C_8H_6N_5O^-$ requires 188.0, found 187.9; $[M+H]^+$ $C_8H_8N_5O^+$ requires 190.0, found 189.9. **4-azo-(3-carboxyl-1,2,4-triazolyl) phenol**. Yellow solid; 81% (3.775g, 0.0162mol) yields, (based on 2.56g, 0.02 mol 3-carboxyl-5-amino-1,2,4-triazole). Anal. Calcd. of $C_9H_{11}N_5O_5$ (%): C, 40.11; H, 4.09; N, 26.00. Found(%): C, 40.08; H, 4.10; N, 25.96. FT-IR (KBr, cm^{-1}): 3335s, 1644s, 1549m, 1436s, 1337m, 1267m, 1145s, 1025m, 843m, 764w, 649w, 528m. ^1H NMR (400 MHz, DMSO) δ 7.82 (d, J=8.8 Hz, 2H), 6.98 (d, J=8.8 Hz, 2H), MS (ESI) m/z $[M-H]^-$ $C_9H_{11}N_5O_5^-$ requires 232.0, found 231.9. **4-azo-(1,2-pyrazolyl) phenol**. Brown solid; 78% (2.933g, 0.0156mol) yields, based on 1.66g, 0.02mol 3-aminopyrazole. Anal. Calcd. of $C_9H_8N_4O$ (%): C, 57.44; H, 4.28; N, 29.77. Found(%): C, 57.46; H, 4.23; N, 29.85. FT-IR (KBr, cm^{-1}): 3256s, 1591s, 1478s, 1376s, 1246s, 1148s, 1093m, 1059m, 1004m, 844s, 778s, 609m, 532m. ^1H NMR (400 MHz, DMSO) δ = 13.32 (s, 1H), 10.27 (s, 1H), 7.83 (s, 1H), 7.76 (d, J=8.1 Hz, 2H), 6.94 (d, J=8.2 Hz, 2H), 6.48 (s, 1H), MS (ESI) m/z $[M-H]^-$ $C_9H_7N_4O^-$ requires 187.0, found 187.0; $[M+H]^+$ $C_9H_9N_4O^+$ requires 189.0, found 188.9. **5-azo-(1,2,4-triazolyl) acetylsalicylic acid**. Pale yellow solid; 67% (3.685g, 0.0134mol) yields, based on 1.68g, 0.02mol 3-amino-1,2,4-triazole. Anal. Calcd. of $C_{11}H_9N_5O_4$ (%): C, 48.00; H, 3.30; N, 25.45. Found(%): C, 47.96; H, 3.31; N, 25.42. FT-IR (KBr, cm^{-1}): 3116s, 2913s, 1673s, 1587s, 1485s, 1446m, 1344m, 1266m, 1227s, 1188s, 981m, 801m, 757m, 675m, 561m. MS (ESI) m/z $[M-2H]^{2-}$ $C_{11}H_7N_5O_4^{2-}$ requires 137.60, found 137.22.

General procedure for the synthesis of the [1,2,4] triazine core: A mixture of reaction substrate (0.1 mmol), catalysts (0.05 mmol), and deionized water (15 mL) was heated in a 25 mL Teflon-lined autoclave at 160℃ for 72 h, followed by slow cooling (5 ℃·h^{-1}) to room temperature. The compounds of **1**-**6** were obtained.

[1,2,4]triazolo[5,1-c][1,2,4]benzotriazine-8-ol (**1**). Yellow crystal, 83% (0.0666 g, 0.083 mmol) yield (based on 0.4 mmol 5-azo-(1,2,4-triazolyl) salicylic acid) Anal. Calcd. for **1** of

Table 1. Optimization of reaction conditions



Entry	Time (h)	Temp. [℃]	Yield (%)(i-v)				
1	72	160	82(i)	81(ii)	79(iii)	73(iv)	71(v)
2	48	160	76(i)	75(ii)	74(iii)	68(iv)	66(v)
3	24	160	68(i)	67(ii)	64(iii)	58(iv)	59(v)
4	72	140	78(i)	78(ii)	77(iii)	69(iv)	68(v)
5	72	120	75(i)	74(ii)	73(iii)	66(iv)	65(v)

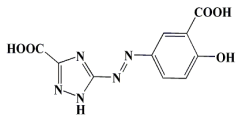
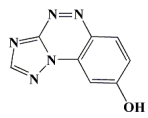
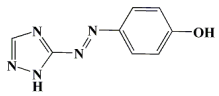
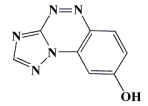
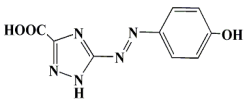
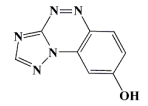
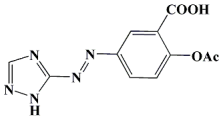
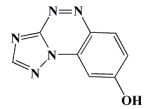
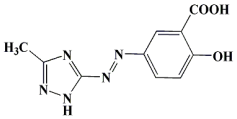
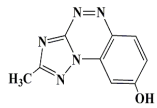
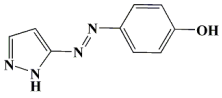
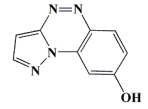
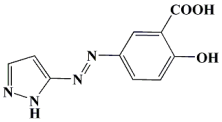
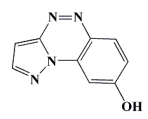
i-v: catalysts (i = $MnCl_2$, ii = $ZnCl_2$, iii = $CdCl_2$, iv = $Dy(OAc)_3$, v = $Tb(OAc)_3$). The calculated yields are based on TBT from the crystals and power products.

$C_{32}H_{26}N_{20}O_7$ (%): C, 47.84; H, 3.24; N, 34.88. Found (%): C, 47.83; H, 3.28; N, 34.86. FT-IR (KBr, cm^{-1}): 3428s, 3039s, 1619s, 1540m, 1511s, 1473w, 1403m, 1344s, 1309s, 1279m, 1233s, 1213s, 1152s, 857m, 668w, 502w. ^{1}H NMR (400 MHz, DMSO) δ 12.15 (s, 1H), 8.90 (s, 1H), 8.64 (d, J = 9.1 Hz, 1H), 7.67 (s, 1H), 7.44 (d, J = 9.1 Hz, 1H), MS (ESI) m/z found $[M-H]^-$ 185.7, $C_8H_4N_5O^-$ requires 186.0. $[M(TBT)_2(H_2O)_4]\cdot 2H_2O$ (M = Mn (**2**), Zn(**3**), Cd(**4**)). **2**: Yellow crystal, 83% (0.0414 g, 0.083 mmol) yield (based on 0.2 mmol 5-azo-(1,2,4-triazolyl) salicylic acid). Anal. Calcd. for **2** of $C_{16}H_{16}N_{10}O_6Mn$ (%): C, 38.45; H, 3.20; N, 28.04. Found (%): C, 38.47; H, 3.19; N, 28.06. FT-IR (KBr, cm^{-1}): 3164s, 1609s, 1539m, 1483m, 1417m, 1365s, 1282w, 1241m, 1221m, 1180m, 1150m, 1109w, 1025m, 858m, 750m, 639w, 514m; **3**: Yellow crystal, 82% (0.0418 g, 0.082 mmol) yield (based on 0.2 mmol 5-azo-(1,2,4-triazolyl) salicylic acid). Anal. Calcd. for **3** of $C_{16}H_{16}N_{10}O_6Zn$ (%): C, 37.66; H, 3.14; N, 27.46. Found (%): C, 37.67; H, 3.13; N, 27.47. FT-IR (KBr, cm^{-1}): 3173s, 1610s, 1539s, 1484s, 1419s, 1364s, 1286m, 1240s, 1218s, 1180m, 1148m, 1109w, 1026m, 855m, 750m, 639w, 514m; **4**: Yellow crystal, 81% (0.0451 g, 0.081 mmol) yield (based on 0.2 mmol 5-azo-(1,2,4-triazolyl) salicylic acid). Anal. Calcd. for **4** of $C_{16}H_{16}N_{10}O_6Cd$ (%): C, 34.51; H, 2.90; N, 25.16. Found (%): C, 34.58; H, 2.83; N, 25.27. FT-IR (KBr, cm^{-1}): 3154s, 1610s, 1540s, 1485s, 1420s, 1366s, 1284m, 1242s, 1219s, 1180m, 1148m, 1108w, 1026m, 857m, 749m, 639w, 513m. 5-methyl-[1,2,4]triazolo[5,1-c][1,2,4]benzotriazine-8-ol (**5**). Yellow crystal, 72% (0.0303 g, 0.072 mmol) yield (based on 0.2 mmol 5-azo-(3-methyl-1,2,4-triazolyl) salicylic acid). Anal. Calcd. for **5** of $C_{18}H_{16}N_{10}O_3$ (%): C, 51.38; H, 3.81; N, 33.30. Found (%): C, 51.40; H, 3.80; N, 33.31. FT-IR (KBr, cm^{-1}): 3177s, 3067s, 1615s, 1471s, 1369s, 1328m, 1257s, 1197s, 1153s, 1116m, 1064m, 846s, 775m, 670m, 613m, 542m. MS (ESI) m/z $[M-H]^-$ $C_9H_6N_5O^-$ requires 200.2, found 199.9. ^{1}H NMR (300 MHz, DMSO) δ 10.41 (s, 1H), 7.77 (d, J = 8.6 Hz, 1H), 6.93 (d, J = 8.6 Hz, 2H), 2.41 (s, 3H). pyrazolo[5,1-c][1,2,4]benzotriazine-8-ol (**6**). Brown solid; 70% (0.0263 g, 0.14 mmol) yield (based on 0.2 mmol 5-azo-(1,2-pyrazolyl) salicylic acid). Anal. Calcd. for **6** of $C_9H_6N_4O$ (%): C, 58.06; H, 3.25; N, 30.09. Found (%): C, 58.04; H, 3.26; N, 30.05. FT-IR (KBr, cm^{-1}): 3254s, 1591s, 1477s, 1375m, 1245s, 1147s, 1092m, 1059m, 1003m, 844m, 775m, 610m, 531m. ^{1}H NMR (400 MHz, DMSO) δ 13.45 (s, 1H), 8.29 (s, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.86 (s, 1H), 7.16 (d, J = 8.9 Hz, 1H), 6.56 (s, 1H), MS (ESI) m/z $[M-H]^-$ $C_9H_5N_4O^-$ requires 185.0, found 184.9.

Results and discussion

The cyclization of azo conjugated aromatic compounds were optimized using 5-azo-(1,2,4-triazolyl) salicylic acid as a model substrate (Table 1). The substrate readily underwent conversion to give TBT crystals when lanthanide metal salts of $Ln(OAc)_3$ were employed as homogeneous catalysts under hydrothermal synthetic conditions. However, when transition metal salts of MCl_2 were employed as homogeneous catalysts under the same hydrothermal synthetic conditions, the same precursor gave TBT complexes crystals of $[M(TBT)_2(H_2O)_4]\cdot 2H_2O$. But the same crystal products of TBT were readily obtained when the complex crystals of $[M(TBT)_2(H_2O)_4]\cdot 2H_2O$ were dissolved in 2 $mol\cdot dm^{-3}$ HCl solution and underwent recrystallization. Screening of the transition and lanthanide metal salts of i-v revealed lanthanide metal salts afforded superior results based on the directly obtained product of TBT. Controlled experiments confirmed that no cyclization reactions were observed in the absence of the metal salts as catalysts or using $CuCl_2$ as the catalyst. With salts of i-v as catalysts, the effect of temperature and reaction time were studied, and the 160 □ and 72h afforded the best results. When reaction temperatures were controlled in the range from 120 to 140 □, the powder products with lower yields were obtained. From the results described above we conclude that the optimal reaction conditions call for the use of MCl_2 or $Ln(OAc)_3$ in water at 160 □ for 72 h under

Table 2. Cyclization of seven others azo conjugated aromatic compounds.

Entry	Substrates	Products	Yields (%) (a-e)
1			83(i),82(ii), 81(iii),80 (iv), 79 (v)
2			69(i),68(ii), 66(iii),66 (iv), 65 (v)
3			67(i),65(ii), 62 (iii), 68 (iv), 69 (v)
4			56(i),55(ii), 51(iii),50 (iv), 51 (v)
5			72(i),71(ii), 70(iii),68 (iv), 67 (v)
6			63(i),62(ii), 60 (iii), 61 (iv), 60 (v)
7			70(i),69(ii), 68 (iii), 65 (iv), 63 (v)

one-step hydrothermal condition.

Under the optimal reaction condition, the scope of the substrates and the generality of the protocol were also studied (Table 2). When 5-azo-(3-carboxyl-1,2,4-triazolyl) salicylic acid, 4-azo-(1,2,4-triazolyl) phenol, 4-azo-(3-carboxyl-1,2,4-triazolyl) phenol and 5-azo-(1,2,4-triazolyl) acetylsalicylic acid served as reaction substrates, the same products of TBT were obtained in good yields. When 5-azo-(3-methyl-1,2,4-triazolyl) salicylic acid served as reaction substrate, a novel organic cyclization product of 5-methyl-[1,2,4]triazolo[5,1-c][1,2,4]benzotriazine-8-ol (MTBT) of $C_{18}H_{16}N_{10}O_3$ (**5**) was obtained with 67-72% yields. When 4-azo-(1,2-pyrazolyl) phenol and 5-azo-(1,2-pyrazolyl) salicylic acid served as reaction substrates, the power product of PBT was obtained. The products of **1**-**5** are confirmed by X-ray crystallographic analysis (Fig. 1 and Fig. S1, ESI†).

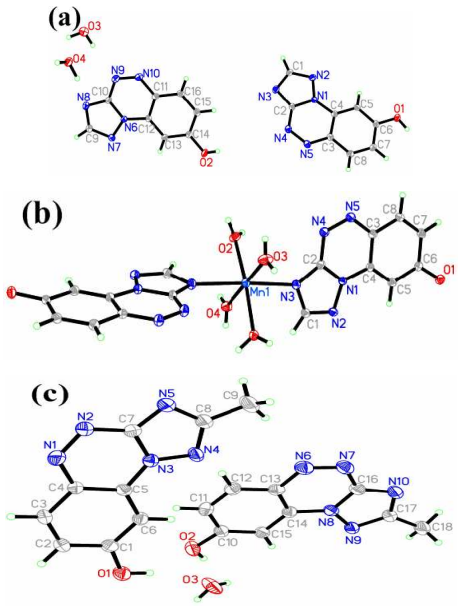


Fig. 1 (a), (b) and (c) ORTEP drawing of **1**, **2** and **5**.

The atomic labeling diagrams of **1** and **2** are shown in Fig. 1a, b, respectively. Each unit cell of **1** contains four fundamental TBT molecules and three lattice water molecules. The bond length of N1-C4 and N6-C12 for triazine ring are 1.371(2) 1.3731(19), respectively. The bond length of C6-O1 and C14-O2 are 1.350(7) and 1.330(7) Å, respectively, indicating an enol former. The TBT is coplanar with dihedral angle of 2.26° between the triazole and phenyl ring. A face-to-face alignment between the aromatic rings with the separated interplanar center-to-center distance of 3.41 to 3.45 Å exhibits a π–π stacking interaction (Fig. S2a, ESI†). Two kinds O-H···O and O-H···N hydrogen-bonds with the O···O and O···N distances of 2.620 to 2.913 Å and the π-π stacking interaction are responsible for the stabilization of the supramolecular structure (Fig. S2a, ESI†). In **2**, each Mn^{2+} ion coordinates to two nitrogen atoms from two triazole moieties and four water molecules to form an octahedral geometry. The bond length of N1-C4 for triazine ring is 1.3721(18). A π-π stacking interaction with the separated interplanar center-to-center distance of 3.371 to 3.382 Å and two kinds O-H···O and O-H···N hydrogen-bonds with the O···O and O···N distances of 2.672 to 2.901 Å are observed. (Fig. S2b, ESI†) Complexes **3** and **4** are isostructural with **2** and their atomic labeling and molecular packing diagrams see Fig. S1 and S3, ESI†. The atomic labeling diagram of **5** is shown in Fig. 1c. Each unit cell of **5** contains two fundamental MTBT molecules and a lattice water molecule. The bond length of C5-N3 and C14-N8 are 1.363(3) and 1.369(3), respectively. A π–π stacking interaction between the aromatic rings with the separated interplanar center-to-center distance of 3.41 to 3.45 Å is also observed in **5** (Fig. S4, ESI†).

The above reaction mechanism for synthesis of 1,2,4-triazine core can be demonstrated by β-hydride elimination that are similar to Pd catalyzed Wacker-type cyclization to generate the carbazole.[4] The proposed catalytic cyclization using 5-azo-(1,2,4-triazolyl) salicylic acid as a model reaction substrate is shown in Scheme S1, ESI†. The reaction pathway may undergo a decarboxylation and an azolated amide-directed Wacker-type cyclization via transition or lanthanide metal homogeneous catalytic reactions under 120-160□ hydrothermal condition.

Fig. 2a and b show a room-temperature photoluminescent emission peak around 500 nm for two aqueous solutions of **1** with a concentration of 10^{-4} mol·dm^{-3} under 290 nm excitation. The left blue lines show the excitation spectra with the monitored incident beam at 500 nm. Insert gives the green fluorescent imaging observed by fluorescence microscope under blue light excitation. The aqueous solutions of **2**-**6** display similar photoluminescent properties with **1** (Fig. S5, ESI†). The photoluminescent spectra for the solid phase of **1** are depicted in Fig. 2b. Under 460 nm blue light excitation, the solid phase of **1** exhibits two maximum emissive peaks around 560 and 670 nm and the observed green-yellow and red imaging taken by the fluorescence microscopy under blue and green light excitation have confirmed the multi-colour fluorescent properties. The compounds of **2**-**6** show similar photoluminescent properties with **1** (Fig. S6, ESI†).

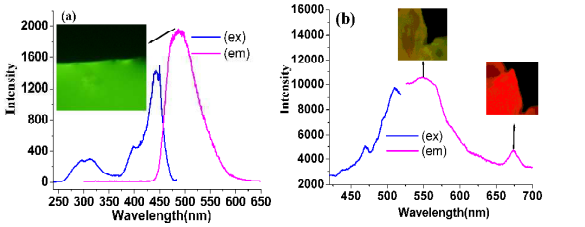


Fig. 2 (a) The photoluminescent spectra of the aqueous solutions of **1**. Insert is fluorescent imaging under blue light excitation. (b) The photoluminescent spectra of crystal phase of **1**. Insert is fluorescent imaging of solid phase under blue and green light excitation.

The time dependent density functional theory (TD-DFT) calculations at B3LYP/6–31G* level has been used to

demonstrate the characteristic excitation spectra of the solid of **1** displays two maximum absorption peaks around 221 and 316 nm, which are attributed to the HOMO-2→LUMO+2 and HOMO→LUMO+1 electronic transitions from enol isomer, respectively (Fig. S7a, b, ESI†). The calculated blue (466 nm) and green (525 nm) absorption peaks for the solid phase of **1** are attributed to the HOMO→LUMO electronic transitions for two different keto isomers that come from the excited-state enol* to keto* proton transfer under UV-vis excitation, in which an intramolecular O-H proton transfer to two different N atoms of triazole ring (Fig. 3a, b).

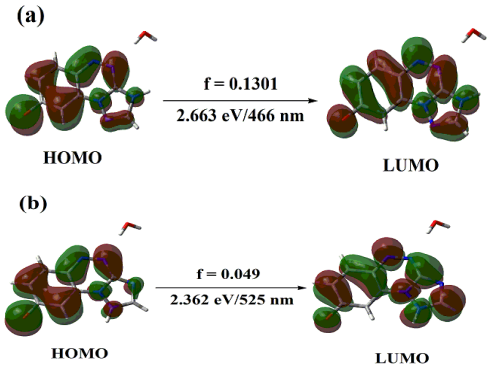


Fig. 3 (a), (b) The TD-DFT calculated state energy diagrams for two different keto isomers in **1**.

Conclusions

In summary, we have developed a novel protocol for the synthesis of the 1,2,4-triazine core via C-H/N-H functionalization followed by intramolecular amination employing MCl_2 or $Ln(OAc)_3$ as catalysts under one-step hydrothermal synthetic condition. This method offers a straightforward access to a wide range of 1,2,4-triazine derivatives, an important structural motif as biological agent in natural and designed compounds. It is also noteworthy for the developed reaction, a feature that should permit further transformation of the 1,2,4-triazine product and provide an entry to structurally diverse heterocycles. In view of the growing understanding of transition or lanthanide-metal-mediated C-H/N-H activation processes, the reaction described herein showcased a reactivity profile that is different to those previously reported. Further study to understand the precise mechanism and to expand the range of substrates as well as to expand their application will be underway in our laboratory.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21271052), Science and Technology Program Foundation of Guangzhou (No.2013J4100016) and Program Foundation of the second batch of innovation teams of Guangzhou Bureau of Education (13C04).

Notes and references

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Electronic Supplementary Information (ESI) available: ^{1}H NMR spectra, X-ray data and crystal structures of **1**–**5**, photoluminescent spectra of **2**-**6**, fluorescent images of **2**-**6**, CCDC 940757 for **1**, 940758 for **2**, 940759 for **3**, 940760 for **4** and 979363 for **5**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/.

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