Electronic Supplementary Material (ESI) for New Journal of Chemistry.

The syntheses, structural and azo-hydrazone tautomeric studies of three triazole/tetrazole azo dyes

Jiawei Cai, Zhixin Li, Yanxuan Qiu, Zhijian OuYang, Wenning Lin, Liu Yang, Weijin Feng, Xinwei Yu and Wen Dong*

School of Chemistry and Chemical Engineering, Guangzhou Key Laboratory for Environmentally Functional Materials and Technology, Guangzhou University, Guangzhou, 510006, China

Table S1. The crystal data and data collection parameters for H_2ATN, $[Ni(H_2AD)_2]\cdot 4H_2O$ and ring-closure product of H_3AD.

	H_2ATN	$[Ni(H_2AD)_2]\cdot 4H_2O$	ring-closure product of H_3AD.
CCDC number	1407822	1410476	1407823
formula	$C_{11}H_8N_6O$	$C_{24}H_{24}N_{10}NiO_8$	$C_{12}H_7N_5O$
Formula weight	240.23	639.22	237.23
Crystal system	monoclinic	trigonal	monoclinic
Space group	$P2_1/n$	$P\text{-}3c1$	$P2_1/n$
a /Å	7.1366(3)	17.1166(4)	3.7787(3)
b /Å	16.9882(6)	17.1166(4)	15.4361(13)
c /Å	9.4410(4)	18.4282(5)	17.0098(14)
α / °	90.00	90.00	90.00
β / °	112.008(2)	90.00	92.735(6)
γ / °	90.00	120.00	90.00
V /Å^3	1061.20(7)	4675.7(3)	991.02(14)
Z	4	6	4
ρ_{calc} mg/mm^3	1.504	1.362	1.590
m /mm^{-1}	0.106	0.682	0.110
F(000)	496.0	1980.0	488.0
Reflections collected	8967	72395	14370
Independent reflections	2437 [R_{int} = 0.0259]	3633 [R_{int} = 0.1394]	2280 [R_{int} = 0.0776]
Goodness-of-fit on F^2	1.017	1.036	0.986
Final R indexes [I>=2σ (I)]	R_1 = 0.0394,[a] wR_2 = 0.0917[b]	R_1 = 0.0686, wR_2 = 0.2009	R_1 = 0.0505, wR_2 = 0.1083
Final R indexes [all data]	R_1 = 0.0682, wR_2 = 0.1051	R_1 = 0.1158, wR_2 = 0.2403	R_1 = 0.1305, wR_2 = 0.1400

[a] $R=\sum||F_o|-|F_c||/\sum|F_o|$. [b] $wR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

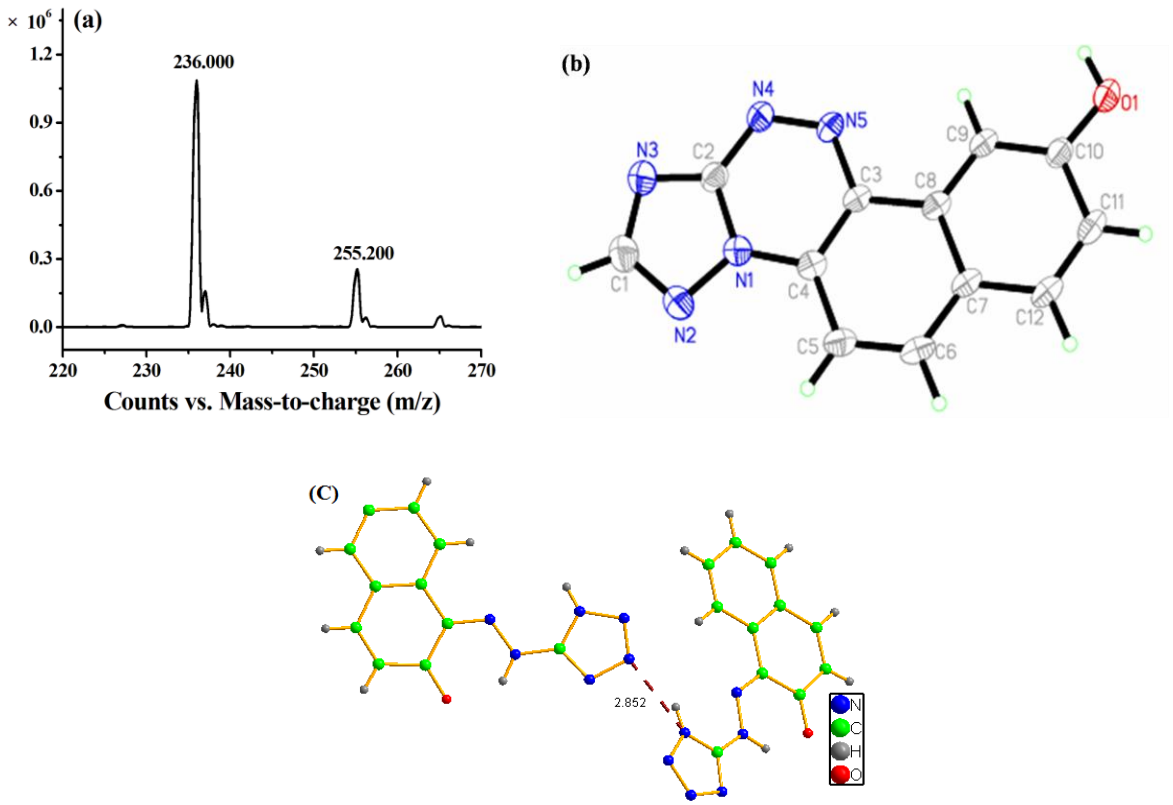
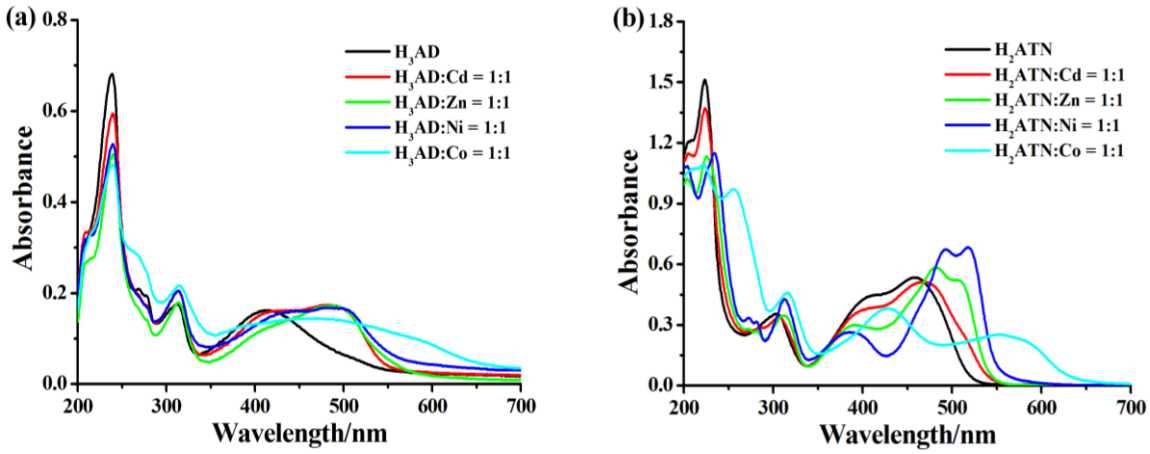


Fig. S1 (a) Mass spectrum for ring-closure product of H_3AD. (b) The atomic labeling diagram for ring-closure product of H_3AD. (c) The intramolecular N–H ···N hydrogen bonding in H_2ATN.



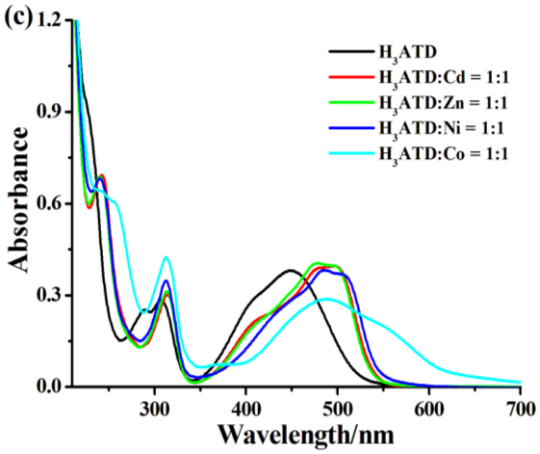


Fig. S2 (a), (b), (c) UV-vis spectra of H_3AD, H_2ATN and H_3ATD and their mixed solution with transition metal ions, respectively.

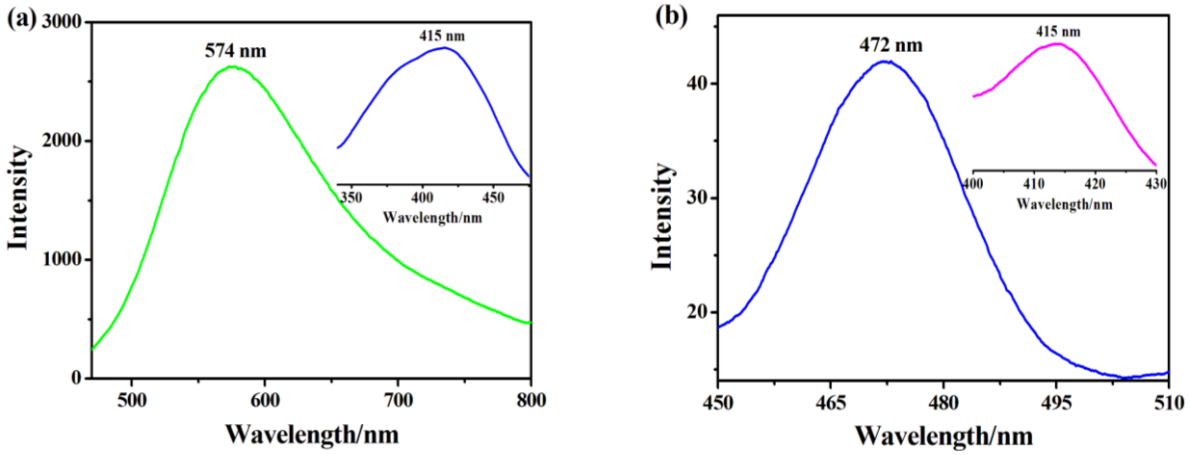


Fig. S3 Room-temperature emission spectra for the neutral ethanol solution (a) and basic ethanol solution (b) of H_3AD with the same concentration.

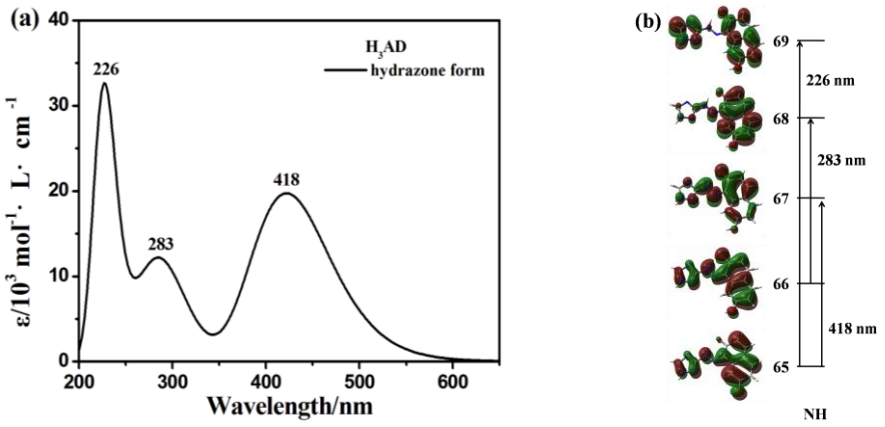


Fig. S4 (a) The calculated electronic spectrum of H_3AD in hydrazone form in aqueous solution. (b) The molecular orbitals involved in the main electronic transitions for hydrazone form of H_3AD.

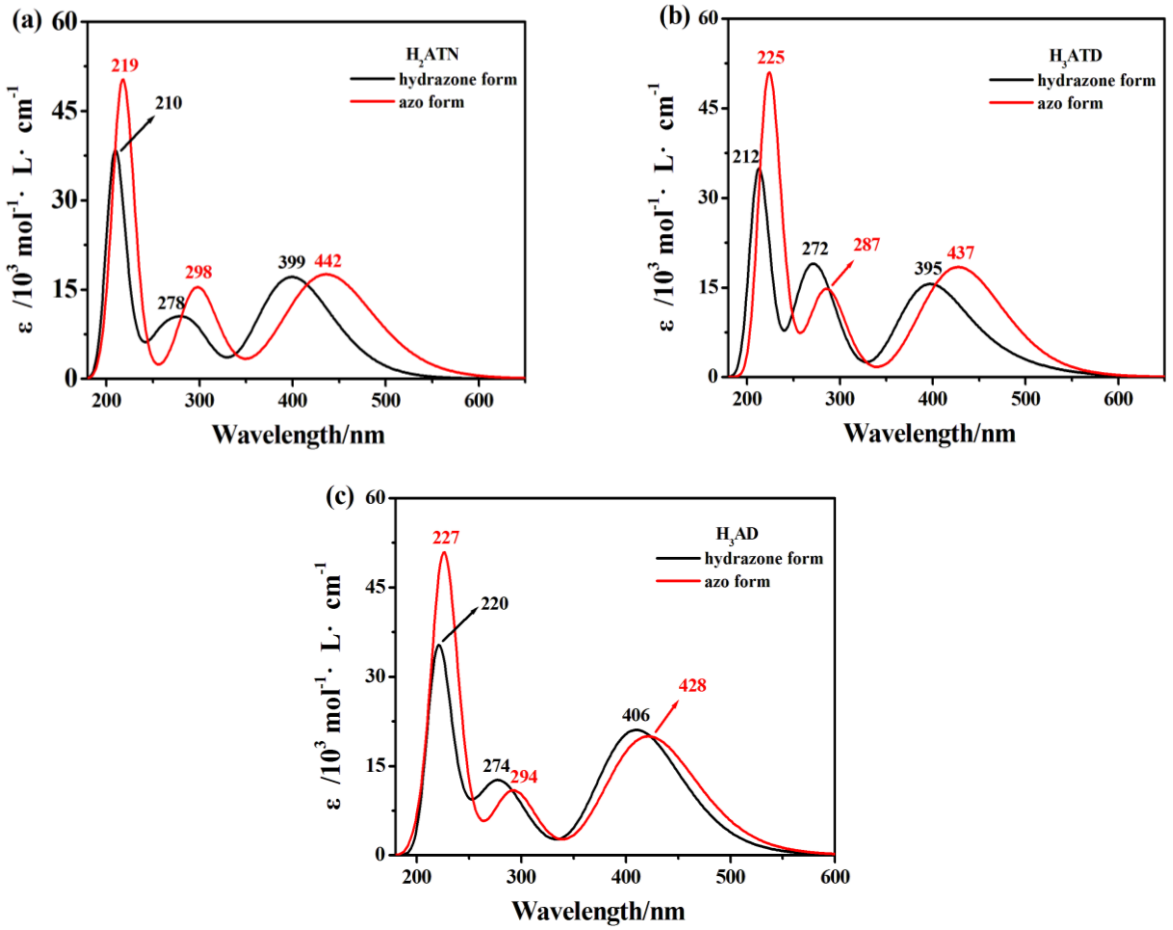


Fig. S5 The calculated electronic spectra of H_2ATN (a), H_3ATD (b) and H_3AD (c) in hydrazone and azo forms in aqueous solution using time dependent density functional theory (TD–DFT) at mPW1PW91/6–311++G(d,p) level.

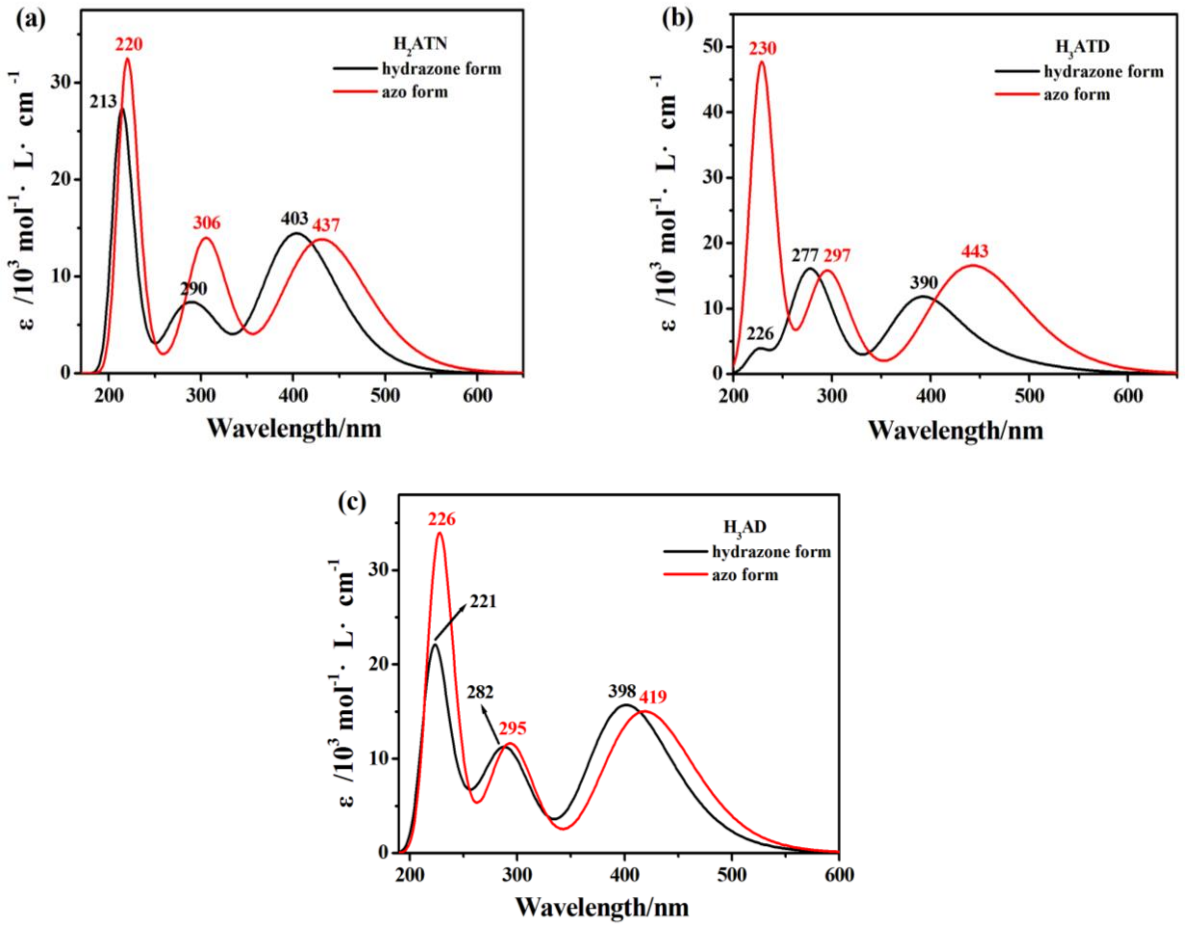


Fig. S6 The calculated electronic spectra of H_2ATN (a), H_3ATD (b) and H_3AD (c) in hydrazone and azo forms in gas phase using time dependent density functional theory (TD–DFT) at B3LYP/6–311++G(d,p) level.