Conventional luminophores often show intense fluorescent emission in dilute solutions but meet with emission quenching in aggregation/solid state, which is widely known as aggregation-caused quenching (ACQ). In recent decades, a class of new functional materials with aggregation-induced emission (AIE) property has emerged as a rising hot topic for their wide applications in organic light-emitting diodes [1, 2], dye-sensitized solar cells [3], bioimaging [4], and cancer theranostics [5]. Exploring the relationships between molecular structures and fluorescence properties are essential for the understanding of the AIE mechanism and designing of the high performance AIE-active materials. The generally accepted explanations for AIE mechanisms are the restriction of intramolecular rotation/vibrations/motions (RIR/RIV/RIM) [6]. In addition to the mechanisms based on molecular geometry, much effort has also been taken to explain the AIE phenomenon based on the electronic effect, such as the restriction of photoinduced twisted intramolecular charge transfer (TICT) [7]. The AIE-active molecules based on RIR, RIV and RIM commonly exhibit twisted molecular configurations which make its synthesis difficult. The structures of TICT-based AIE-active molecules are relatively simple and, in consequence, they are easily obtained [8–10]. Moreover, the combination of AIE and TICT characteristics may produce unique fluorescence performance [11].

In the course of our continuing efforts in understanding the relationship between structure and photoluminescence [12, 13], two coumarin derivatives, 7-diethylamino-3-(4-nitrophenyl)coumarin (DNC) and 7-hydroxy-3-(4-nitrophenyl)coumarin (HNC), were synthesized via Knoevenagel condensation of salicylaldehyde derivatives with 4-nitrophenylacetonitrile and then cyclization reaction. Both of them were characterized by single-crystal X-ray diffraction. The molecules of DNC are stacked via π-π interaction, while the hydrogen bond interactions instead of π-π interaction were observed in the crystal packing of HNC. Both of DNC and HNC showed solvatochromic properties and aggregation-induced emission (AIE) activities, but the AIE characteristics of them were entirely different. HNC exhibited an AIE phenomenon as the result of the restriction of twisted intramolecular charge transfer (TICT), while DNC emitted peculiar dual fluorescence which was assigned to the emission based on the inhibition of TICT state formation and the emission from the TICT state respectively.

**Keywords** Coumarin · TICT · AIE · Fluorescence · Solvatochromic property
state is extremely rare because the molecular aggregation is usually unfavorable for the formation of the photoinduced TICT state.

**Experimental**

**Reagents and apparatus**

All chemicals were obtained from commercial suppliers. 1 H NMR and 13 C NMR spectra were recorded on a Bruker Av 400 NMR spectrometer. ESI-MS spectra were performed on a Bruker Esquire HCT mass spectrometer. Fluorescence spectra were taken on a Hitachi F-7000 fluorescence spectrometer. The X-ray diffraction data was collected on an Agilent Gemini A Ultra diffractometer.

**General synthetic procedure for DNC and HNC**

Salicylaldehyde derivative (4-diethylaminosalicylaldehyde or 4-hydroxysalicylaldehyde, 4 mmol) and 4-nitrophenyl-acetonitrile (0.648 g, 4 mmol) were dissolved in absolute ethanol (5 mL). After a tiny amount of piperidine was added for catalysis, the mixture was stirred for 2 h at 60 °C. A red solid precipitated out. The precipitate was collected by filtration and then washed several times with ethanol (5 mL). After a tiny amount of piperidine was added for catalysis, the mixture was stirred for 2 h at 110 °C during which time a solid precipitated out. The precipitate was collected by filtration and then washed several times with a small amount of ethanol or 4-hydroxysalicylaldehyde, 4 mmol) and 4-nitrophenyl-acetonitrile (0.648 g, 4 mmol) were dissolved in absolute ethanol (5 mL). After a tiny amount of piperidine was added for catalysis, the mixture was stirred for 2 h at 60 °C. A red solid precipitated out. The precipitate was collected by filtration and then washed several times with ethanol (5 mL).

**DNC**

DNC: orange solid, yield: 90.2%, 1 H NMR (400 MHz, DMSO-d6) δ: 8.34 (s, 1 H), 8.27 (d, 2 H, J = 8.2 Hz), 8.04 (d, 2 H, J = 8.2 Hz), 7.56 (d, 1 H, J = 8.2 Hz), 6.78 (d, 1 H, J = 8.2 Hz), 6.60 (s, 1 H), 3.47 (q, 4 H, J = 6.4 Hz), 1.15 (t, 6 H, J = 6.4 Hz), 13 C NMR (100 MHz, DMSO-d6) δ: 159.9, 156.2, 151.2, 145.9, 143.1, 124.2, 143.1, 142.4, 130.3, 128.6, 123.2, 115.8, 109.4, 108.2, 96.0, 44.1, 12.2. ESI-MS m/z calculated for [M-H]− 282.04, found 282.0 (Fig. S4–6).

**HNC**

HNC: yellow solid, yield: 86.5%, 1 H NMR (400 MHz, DMSO-d6) δ: 10.79 (s, 1 H), 8.39 (s, 1 H), 8.29 (d, 2 H, J = 8.8 Hz), 8.01 (d, 2 H, J = 8.8 Hz), 7.65 (d, 1 H, J = 8.8 Hz), 6.85 (dd, 1 H, J1 = 8.8 Hz, J2 = 2.0 Hz), 6.77 (d, 1 H, J = 2.0 Hz). 13 C NMR (100 MHz, DMSO-d6) δ: 162.7, 160.1, 155.9, 147.1, 143.7, 142.4, 131.1, 129.8, 123.8, 120.3, 114.2, 112.2, 102.3. ESI-MS m/z calculated for [M-H]− 282.04, found 282.0 (Fig. S4–6).
in toluene were observed. The emissions of DNC in THF, MeCOOEt and CHCl₃ were so faint that it is hard to be distinguished. In MeCN, EtOH and MeOH, no luminescence was perceived. HNC displayed similar solvatochromic property as DNC. With the increase of the solvent polarity (from petroleum ether to acetonitrile), the emission peak gradually shifted to long-wavelength region and the fluorescence intensity is enhanced except for MeCN in which the emission intensity decreased. In EtOH and MeOH the fluorescence emission was neatly quenched (Fig. 3E). The fluorescence color change from blue to orange was observed when the solvent changed from petroleum ether to acetonitrile. In the more polar solvents such as ethanol and methanol, the fluorescence of HNC was quenched due to the formation of dark TICT state (Fig. 3F).

AIE Properties

The AIE characteristics of DNC and HNC in the binary mixtures of acetonitrile and water with varied volume ratios were investigated. The concentration-dependent fluorescence spectra of HNC and DNC in CH₃CN/H₂O (1:9, V/V) indicated that HNC emitted obvious aggregation-induced fluorescence until its concentration was up to 50 µmol/L, while DNC showed a visible AIE phenomenon at a lower (Table S2). No π–π stacking interactions were found in the crystal packing (Fig. 2B).

Solvatochromic Properties

Both of DNC and HNC are the typical donor-acceptor type luminophores which commonly show solvent-dependent photophysical property [15, 16]. Therefore, the solvent polarity effect on the absorption and emission of them was firstly investigated and the absorption and emission spectra in different solvents are shown in Fig. 3. Both DNC and HNC exhibited abnormal low, short-wavelength absorption in petroleum. In other solvents, the absorbances were similar, and the maximum absorption showed slight changes with the variation of solvent polarity which can be ascribed to the intramolecular charge transfer (ICT) (Fig. 3A and D). The emission peak of DNC appears at 475 nm in petroleum ether, which shifted to 505 nm in toluene due to the solvent-enhanced intramolecular charge transfer. In more polar solvents such as THF, MeCOOEt and CHCl₃ the luminescence intensities of the DNC were dramatically weakened, and even were quenched in MeCN, EtOH and MeOH owning to the conversion from the locally excited state to the dark twisted intramolecular charge transfer state (Fig. 3B). The emission colors of DNC in different solvents under 365 nm UV lamp were illustrated in Fig. 3C. The blue luminescence in petroleum ether and the strong green luminescence

![Fig. 1](A) Crystal structure of DNC shown at 50% probability. (B) Crystal packing showing one-dimensional molecular chain along b-axis via π–π stacking interaction

![Fig. 2](A) Crystal structure of HNC shown at 50% probability. (B) Crystal packing viewed along a-axis

![Fig. 3](Absorption spectra of DNC (A) and HNC (D) in different solvents. Fluorescence spectra of DNC (B) and HNC (E) in different solvents. Photographs of DNC (C) and HNC (F) in different solvents taken in a dark-box ultraviolet analyzer when excited at 365 nm. 10 µmol/L HNC and DNC were used for all the spectral measurement and the photoshoots

Fig. 3 Absorption spectra of DNC (A) and HNC (D) in different solvents. Fluorescence spectra of DNC (B) and HNC (E) in different solvents. Photographs of DNC (C) and HNC (F) in different solvents taken in a dark-box ultraviolet analyzer when excited at 365 nm. 10 µmol/L HNC and DNC were used for all the spectral measurement and the photoshoots

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emission enhancement at 495 nm. The appearance of the dual fluorescence should be ascribed to the formation of molecular aggregates, which was further supported by the absorption changes in MeCN/H₂O mixtures when the water volume fractions were higher than 60% (Fig. S9B). Unfortunately, the AIE effect of DNC was inconspicuous on account of the π-π stacking interaction in the aggregates of DNC (Fig. 1B). The shorter-wavelength emission (495 nm) of the dual fluorescence was assigned to the relaxation of the locally excited state, while the longer-wavelength emission (625 nm) should be ascribed to the radiative relaxation of TICT state. It suggested that the aggregation cannot entirely inhibit the TICT state formation of DNC, and the TICT state in the aggregation state tend to relax back to the ground state via radiative channel. The TICT fluorescence in solution is rarely observed because the TICT state often relaxes back to the ground state via nonradiative pathways [15]. The aggregation-state TICT fluorescence is rarer because the molecular aggregation generally cause the restriction of the photoinduced TICT state formation [24]. On the contrary, the aggregation-induced TICT restriction can commonly lead to local fluorescence [16]. Therefore, the aggregation-state TICT fluorescence of DNC is a very interesting finding.

The photos of DNC and HNC in solid states under UV/natural light irradiation were shown in Fig. 5. DNC was orange under natural light (Fig. 5 C). When excited by UV irradiation, it emitted strong red fluorescence both in the crystal state and in the powder state (Fig. 5 A and 5 B), whereas the aggregation-induced fluorescence in MeCN/H₂O solutions with water fractions between 10% and 70%, little changes in emission spectra were observed. When the water fraction was increased to 80%, the fluorescence intensity was distinctly enhanced and accompanied by a little blue shift, which was ascribed to the fact that the formation of the molecular aggregates inhibited the formation of TICT state and thereby local fluorescence appeared. The absorption curves of HNC tended to be flatter and broader when the water fractions were up to 80%, which was a further proof of the aggregate formation of HNC (Fig. S9A). Unlike HNC exhibiting AIE characteristics based on the TICT mechanism that has been widely reported [17–23], DNC exhibited peculiar dual fluorescence in the aggregate state. As shown in Fig. 4D–F, DNC emitted weak green fluorescence at 485 nm in pure acetonitrile. Upon adding water, the emission intensities were reduced slightly and about 10 nm red-shift was observed. When increasing the water fraction from 60 to 99%, a new emission peak at about 625 nm emerged, which was companied by a slight emission enhancement at 495 nm. The appearance of the dual fluorescence should be ascribed to the formation of molecular aggregates, which was further supported by the absorption changes in MeCN/H₂O mixtures when the water volume fractions were higher than 60% (Fig. S9B).

Fig. 4 Fluorescence spectra of HNC (A) and DNC (D) in MeCN/H₂O mixtures with different water fractions. Plots of fluorescence intensity versus water fraction for HNC (B) and DNC (E). Photographs of HNC (C) and DNC (F) in MeCN/H₂O with different water fractions under 365 nm UV irradiation. The concentrations of HNC and DNC are 50 µmol/L and 10 µmol/L respectively.
emit TICT fluorescence because the tight, regular molecular arrangement in crystal lattices restricts the molecular geometry changes in the formation of the TICT state. Hence the TICT fluorescence in solid state is extremely rare except for the particular-shaped molecules [25]. HNC in solid states was yellow under natural light (Fig. 3 F). Under UV light excitation it emitted green fluorescence both in crystal and powder state as observed in MeCN/H$_2$O mixtures (Figs. 4 and 5D and E C).

Conclusions

In summary, we have obtained two coumarin-based donor-acceptor type luminophores, which were briefly named as DNC and HNC, through a facial synthetic strategy. HNC exhibited typical AIE characteristics based on the mechanism of the restriction of TICT state formation in the aggregate state. Significantly, DNC in aggregate state emitted dual fluorescence which was ascribed to the emission based on the restriction of TICT state formation and the TICT emission respectively. The TICT emission in the aggregate state is very rare.

Supplementary information The online version contains supplementary material available at https://doi.org/10.1007/s10895-022-02933-2.

Author contributions EW contributed to the study conception and design, and was the major contributor in writing the manuscript. The synthesis, spectrum test, data analysis and so on were performed by QL with the assistance of YZ. The X-ray diffraction data collection and structure determination was performed by ZN.

Funding This work is financially supported by the National Natural Science Foundation of China (22061016) and Program for Innovative Research Team in University (IRT-16R19).

Availability of data and material/Data availability The crystallographic information files that have been deposited in the Cambridge Crystallographic Data Centre (CCDC 2,130,543 for DNC and 2,130,544 for HNC) which are freely available for all. The link for CCDC: https://www.ccdc.cam.ac.uk/.

Code Availability not applicable.

Declarations

Conflicts of Interest/Competing interests The authors have no conflicts of interest to declare that are relevant to the content of this article.

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

References

1. Cai Y, Qin A, Tang BZ (2017) Siloles in optoelectronic devices. J Mater Chem C 5:7375–7389. https://doi.org/10.1039/C7TC02511D
2. Liu D, Wei JY, Tian WW, Jiang W, Sun YM, Zhao Z, Tang BZ (2020) Endowing TADF luminophors with AIE properties through adjusting flexible dendrons for highly efficient solution-processed nondoped OLEDs. Chem Sci 11:7194–7203. https://doi.org/10.1039/D0SC02194F
3. Li CT, Kuo YL, Kumar CHP, Huang PT, Lin JT (2019) Tetraphenylethylene tethered phenothiazine-based double-anchored sensitizers for high performance dye-sensitized solar cells. J Mater Chem A 7:23225–23233. https://doi.org/10.1039/C9TA09025H
4. Qian J, Tang BZ (2020) AIE luminogens for bioimaging and theranostics: from organelles to animals. Chem 3:56–91. https://doi.org/10.1034/j.1651-2048.2017.05.010
5. Gao M, Tang BZ (2020) AIE-based cancer theranostics. Coordn Chem Rev 402:213076. https://doi.org/10.1016/j.ccr.2019.213076
6. Mei J, Leung NLC, Kwok RTK, Lam JWY, Tang BZ (2015) Aggregation-induced emission: together we shine, united we soar. Chem Rev 115:11718–11940. https://doi.org/10.1021/acs.chemrev.5b00263
7. Gao BR, Wang HY, Hao YW, Fu LM, Fang HH, Jiang Y, Wang L, Chen QD, Xia H, Pan LY, Ma YG, Sun HB (2010) Time-resolved fluorescence study of aggregation-induced emission enhancement by restriction of intramolecular charge transfer state. J Phys Chem B 114:128–134. https://doi.org/10.1021/jp909063d
8. Abedi SAA, Chi W, Tan D, Shen T, Wang C, Ang ECX, Tan CH, Anariba F, Liu X (2021) Restriction of twisted intramolecular charge transfer enables the aggregation-induced emission of 1-(N,N-dialkylamino)-naphthalene derivatives. J Phys Chem A 125:8397–8403. https://doi.org/10.1021/acs.jpc.a102586
9. Li J, Qian Y, Xie L, Yi Y, Li W, Huang W (2011) Restriction of photoinduced twisted intramolecular charge transfer. ChemPhysChem 12:397–404. https://doi.org/10.1002/cpdc.201000457
10. Li J, Qian Y, Xie L, Yi Y, Li W, Huang W (2015) (1) From dark TICT state to emissive quasi-TICT state: the AIE mechanism of N-(3-(benzo[d]oxazol-2-yl)phenyl)-4-tert-butylbenzamide. J Phys Chem C 119: 2133–2141. https://doi.org/10.1021/jp5089433
11. Chiang Y, Lai Z, Chen C, Chang C, Liu B (2018) Construction of emission-tunable nanoparticles based on a TICT-AIEgen: Impact of aggregation-induced emission versus twisted intramolecular charge transfer. J Mater Chem B 6:2869–2876. https://doi.org/10.1039/C8TB00539G
12. Li Q, Niu ZG, Liu YL, Wang EJ (2020) Crystal structure and aggregation-induced emission of an azine derivative. Chin J Struct Chem 39:693–697. https://doi.org/10.14102/j.cnki.0254-5861.2021-2464
13. Zhang ZY, Niu ZG, Wang EJ (2019) (1) Chemical conversion of a coumarin derivative containing aroylhydrazono: crystal structures and fluorescence properties. Chin J Struct Chem 38:384–389. https://doi.org/10.14102/j.cnki.0254-5861.2011-2098
14. Sheldrick GM (2014) SHELXL-2014/7. Program for the Solution of Crystal Structures. University of Göttingen, Göttingen
15. Sasaki S, Drummen GPC, Konishi G (2016) (1) Recent advances in twisted intramolecular charge transfer (TICT) fluorescence and related phenomena in materials chemistry. J Mater Chem C 4:2731–2743. https://doi.org/10.1039/C5TC03933A
16. Sun H, Tang XX, Miao BX, Yang Y, Ni Z (2018) (1) A new AIE and TICT-active tetraphenylethylene-based thiazole compound: synthesis, structure, photophysical properties and
application for water detection in organic solvents. Sens Actuat B-Chem 267: 448–456. https://doi.org/10.1016/j.snb.2018.04.022

17. Wang DH, Chen LJ, Zhao X, Yan XP (2021) Enhancing near-infrared AIE of photosensitizer with twisted intramolecular charge transfer characteristics via rotor effect for AIE imaging-guided photodynamic ablation of cancer cells. Talanta 225:122046. https://doi.org/10.1016/j.talanta.2020.122046.

18. Hu R, Lager E, Aguilar-Aguilar A, Liu J, Lam JWY, Sung HHY, Williams ID, Zhong Y, Wong KS, Peña-Cabrera E, Tang BZ (2009) Twisted Intramolecular Charge Transfer and Aggregation-Induced Emission of BODIPY Derivatives. J Phys Chem C 113:15845–15853. https://doi.org/10.1021/jp902962h.

19. Zhang J, Xu B, Chen J, Wang L, Tian W (2013) Oligo(phenothiazine): twisted intramolecular charge transfer and aggregation-induced emission. J Phys Chem C 117:23117–23125. https://doi.org/10.1021/jp405664m.

20. Sun H, Tang XX, Miao BX, Yang Y, Ni Z (2018) A new AIE and TICT-active tetraphenylethene-based thiazole compound: synthesis, structure, photophysical properties and application for water detection in organic solvents. Sens Actuat B-Chem 267:448–456. https://doi.org/10.1016/j.snb.2018.04.022

21. Sun H, Tang XX, Zhang R, Sun WH, Miao BX, Zhao Y, Ni ZH (2020) Tetraphenylethene-substituted benzothiadiazoles: AIE and TICT properties, tunable intramolecular conjugation and application in detecting trace water in organic solvents. Dyes Pigm 174:108051. https://doi.org/10.1016/j.dyepig.2019.108051

22. Hu Q, Gong T, Mao Y, Yin Q, Wang Y, Wang H (2021) Two-phase activated colorimetric and ratiometric fluorescent sensor for visual detection of phosgene via AIE coupled TICT processes. Spectrochim Acta A 253:119589. https://doi.org/10.1016/j.saa.2021.119589

23. Jiang M, Gu X, Lam JWY, Zhang Y, Kwok RTK, Wong KS, Tang BZ (2017) Two-photon AIE bio-probe with large stokes shift for specific imaging of lipid droplets. Chem Sci 8:5440–5446. https://doi.org/10.1039/C7SC01400G

24. Zhao Y, He S, Yang J, Sun H, Shen X, Han X, Ni Z (2018) Study on TICT emission of TPE-BODIPY derivatives mediated by methyl group on BODIPY. Opt Mater 81:102–108. https://doi.org/10.1016/j.optmat.2018.05.023

25. Naito H, Nishi K, Morisaki Y, Tanaka K, Chujo Y (2016) Solid-state emission of the anthracene-o-carborane dyad from the twisted-intramolecular charge transfer in the crystalline state. Angew Chem Int Ed 55:1–7. https://doi.org/10.1002/anie.201609656

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