1,8-Naphthalimide-Based Highly Emissive Luminophors with Various Mechanofluorochromism and Aggregation-Induced Characteristics

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Supporting Information

ABSTRACT: Six 1,8-naphthalimide-based tetraphenylethene derivatives were reported. These highly solid-state emissive compounds showed aggregation-induced emission enhancement or aggregate fluorescence change characteristics. Furthermore, these aggregation-induced green light-emitting or aggregation-induced yellow light-emitting luminophors also exhibited various mechanofluorochromism behaviors involving different fluorescent color changes. To determine the mechanochromic mechanism of these six mechanical stimulus-responsive luminogens, the powder X-ray diffraction (XRD) and X-ray single-crystal measurements were carried out. The powder XRD test results indicated that their interesting mechanofluorochromic behaviors were attributed to the interconversion between crystalline and amorphous states. Meanwhile, the X-ray single-crystal analyses results implied that the twisted molecular conformation and the absence of an intense intermolecular acting force led to a loose packing motif, and the alteration of molecular packing was responsible for the observed mechanofluorochromic effect.

INTRODUCTION

Over the past decades, organic fluorescent materials have attracted increasing attention on account of their fundamental importance and potential applications in photoelectronic devices and fluorescent sensors.1−11 Smart materials with mechanical stimulus-responsive luminescence changing feature are of particular interest. Indeed, considerable effort has been devoted to the exploitation of mechanochromic materials.12−25 To realize the high-contrast mechanochromic phenomenon before and after stimulating, strong solid-state emission is highly desired.26−28 However, emissions of a majority of luminophors are weakened or even quenched when they are in solid or aggregation states, which is caused by the aggregation-caused quenching (ACQ) effect.29−31 Such a notorious and thorny ACQ problem has greatly limited the effective application of mechanochromatic materials. Fortunately, in 2001, an unusual and opposite aggregation-induced emission (AIE) phenomenon was observed by Tang’s group.32 Subsequently, in 2002, Park et al. reported the interesting aggregation-induced emission enhancement (AIEE) effect.33 Instead of emission quenching, fluorescent molecules with AIE or AIEE behavior can emit bright light by aggregate formation.34−36 Meanwhile, luminophors with aggregate fluorescence change feature can also usually emit strong fluorescence in the aggregation state.37−39 Therefore, the discovery of AIE, AIEE, and aggregate fluorescence change phenomena is helpful for the acquisition of high-contrast mechanochromic luminescence materials. On the other hand, the exploitation of novel organic emitters with wide tuning range wavelength based on the same core structure has become a promising and wildly attentional research topic in the last ten years.35−37 1,8-Naphthalimide-based compounds are an important class of organic dyes, and they exhibit potential practical applications in a wide range of fluorescent sensors, optical devices, and fluorescent cellular imaging agents.38−43 Unfortunately, the aggregate-state luminous efficiency of most 1,8-naphthalimide-based luminogens is not ideal owing to the existence of the ACQ effect.44 Indeed, it is significative and challenging to design and synthesize highly solid-state emissive 1,8-naphthalimide-based derivatives. In this work, six highly solid-state emissive luminophors (Chart 1) based on 1,8-naphthalimide and tetraphenylethene units were successfully obtained. Furthermore, compounds 1−3 showed obvious AIEE characteristics involving fluorescent color change from weak orange to strong green. Interestingly, compounds 4−6 showed aggregate fluorescence change feature involving fluorescent color change from orange to yellow. In addition, luminogens 1−3 exhibited reversible mechanofluorochromic phenomena with color changes between blue or blue-green and green emissions. Meanwhile, luminogens 4−6 also exhibited reversible mechanochromic characteristics involving...
flourescent color change from yellow-green or yellow to yellow or orange. Indeed, the preparation of these highly solid-state emissive 1,8-naphthalimide-based luminogens is beneficial to the development of rewritable recording mediums (Scheme 1).

■ RESULTS AND DISCUSSION

AIEE or Aggregate Fluorescence Change Behaviors of Compounds 1–6. To investigate the aggregation-induced properties of compounds 1–6, the corresponding UV–vis absorption spectra in dimethylformamide (DMF)–H₂O mixtures with different water contents were surveyed initially (Figures S1–S6, Supporting Information). Level-off tails could be clearly observed in the long-wavelength region as the water content increased. Such tails can commonly be observed in nanoparticle suspensions and are the signals of the formation of nanoscopic aggregates.⁴⁵ Subsequently, the photoluminescence (PL) spectra were recorded in DMF–H₂O mixtures with various water fractions (f_w). As shown in Figure 1, luminogen 1 displayed very weak emission with λ_max at 609 nm in dilute DMF solution, corresponding to a weak orange fluorescence under 365 nm UV light, and its absolute fluorescence quantum yield (Φ) was 1.44%. However, the emission intensity decreased significantly, and the orange fluorescence almost disappeared as the water content was increased to 10% because of the twisted intramolecular charge-
transfer (TICT) effect.33 Interestingly, when the water content was increased to 50%, a new green emission band was observed with \( \lambda_{\text{max}} \) at 511 nm. Furthermore, the mixture emitted bright green light with a fluorescence quantum yield up to 46.42% when the \( f_w \) value was 90%. Obviously, water is a nonsolvent of compound 1. Therefore, the strong green light-emitting was triggered by the aggregate formation. In fact, the nano-aggregates (\( f_w = 90\% \)) obtained were confirmed by dynamic light scattering (DLS) (Figure 2). The formation of nano-aggregates resulted in the restricted intramolecular rotation of tetraphenylethene unit and thus the generation of the green light emission. Clearly, compound 1 is an AIEE-active luminogen. Similarly, as shown in Figures S7 and S8, compounds 2 and 3 also exhibited excellent AIEE properties. On the other hand, as shown in Figure S9, compound 4 exhibited one emission band with \( \lambda_{\text{max}} \) at 611 nm in dilute DMF solution, and it emitted an orange fluorescence (\( \Phi = 29.02\% \)) under 365 nm UV irradiation. Interestingly, when \( f_w \) reached 20%, the orange fluorescence also almost disappeared, and this phenomenon could also be attributed to the TICT effect. As \( f_w \) was further increased to 50%, one new emission band was observed with \( \lambda_{\text{max}} \) at 558 nm, and the fluorescence color changed from orange to yellow. When \( f_w \) exceeded 50%, the fluorescent color was still yellow, and the fluorescence quantum yield was 31.66% as the \( f_w \) value was increased to 90%. Moreover, when the water content was 90%, the nano-aggregates obtained were also characterized by DLS (Figure 2), and thus compound 4 exhibited interesting aggregate fluorescence change behavior involving a fluorescence color changing from orange to yellow. Similarly, as shown in Figures S10 and S11, compounds 5 and 6 also exhibited aggregate fluorescence change properties.

**Mechanofluorochromic Characteristics of Compounds 1−6.** Next, the mechanochromic fluorescence behaviors of luminogens 1−6 were explored by solid-state PL spectroscopy. As evident from Figure 3, the solid sample of compound 1 emitted bright blue-green light with one emission band at 484 nm (\( \lambda_{\text{max}} \)), and its luminescence quantum yield was 20.82%, and the average lifetime of the as-synthesized sample 1 was 4.04 ns (Figure 4). However, after it was ground using a spatula or a pestle, a green light centered at 517 nm was observed, and the quantum yield of ground sample 1 was 20.16%, and the average lifetime of the ground sample 1 was 4.45 ns. Moreover, the mechanochromic green fluorescence could be converted into its initial state upon treatment with fuming dichloromethane vapor for 1 min. Thus, luminogen 1 showed reversible mechanochromic behavior with fluorescence changes between blue-green and green emissions. Furthermore, the repeatability of this mechanofluorochromic conversion of 1 was superior (Figure 5). Similarly, as shown in Figures 6 and 7, luminogens 2 and 3 also showed reversible mechanochromic fluorescence phenomena involving color changes from blue or blue-green to green, and their corresponding luminescence lifetimes before and after grinding were shown in Figures S12 and S13 (Supporting Information). Meanwhile, their mechanofluorochromic conversion could also be repeated several times without fatigue (Figures S16 and S17, Supporting Information). Obviously, the high-contrast...
mechanochromic fluorescence of 2 affords its potential application in rewritable recording mediums. As shown in Figure 8, we wrote two letters “C” and “Z” on the weighing paper, which exhibited green luminescence in the sheared area. Upon treatment of the ground sample with fuming dichloromethane vapor, the two letters turned to the original blue. On the other hand, as can be seen in Figure 9, luminogen 4 showed an emission band with $\lambda_{\text{max}}$ at 562 nm and emitted strong yellow fluorescence with the quantum yield of 30.16% and the average lifetime of 2.71 ns (Figure 10). In contrast, a slightly red-shifted emission peak centered at 568 nm was observed, and a yellowish brown fluorescence ($\Phi = 29.80\%$) was noticed under 365 nm UV light, and the initial emission state was obtained after treatment with dichloromethane vapor. Therefore, luminogen 4 showed reversible mechanochromic phenomenon involving slightly red-shifted fluorescent color change, and a set of four cycles of repeated grinding-fuming processes is shown in Figure 11. Similarly, as shown in Figures 12 and 13, luminogens 5 and 6 also showed reversible mechanoluminescent characteristics with color changes from yellow or yellow-green to orange or yellow, and their luminescence lifetimes in various solid states were shown in Figures S14 and S15 (Supporting Information), and the repeatabilities of their mechanoluminescent behaviors were good (Figures S18 and S19, Supporting Information). Furthermore, as presented in Figure S20 (Supporting Information), the reversible mechanochromic fluorescence of 6 could also be applied in optical recording. The maximum emission wavelengths of compounds 1–6 in different solid states (as-synthesized powder, ground one and fumed one) have been summarized in a table (Figure S21, Supporting Information).

Powder X-ray Diffraction and X-ray Single-Crystal Measurements. To determine the mechanoluminescent mechanism of 1–6, the powder X-ray diffraction (XRD) patterns of 1–6 in various solid states were measured. Take

Figure 6. (A) PL spectra of luminogen 2 at different conditions. Excitation wavelength: 365 nm. Photographic images of luminogen 2 under 365 nm UV light: (B) as-synthesized solid sample; (C) ground sample; (D) sample after treatment with dichloromethane vapor.

Figure 7. (A) PL spectra of luminogen 3 at different conditions. Excitation wavelength: 365 nm. Photographic images of luminogen 3 under 365 nm UV light: (B) as-synthesized solid sample; (C) ground sample; (D) sample after treatment with dichloromethane vapor.

Figure 8. Repeated writing and erasing processes utilizing the switchable mechanochromic fluorescence of 2.

Figure 9. (A) PL spectra of luminogen 4 at different conditions. Excitation wavelength: 365 nm. Photographic images of luminogen 4 under 365 nm UV light: (B) as-synthesized solid sample; (C) ground sample; (D) sample after treatment with dichloromethane vapor.

Figure 10. Decay curves (excitation wavelength: 365 nm) of luminogen 4 in various solid states: the unground solid sample (the black line, emission wavelength: 562 nm) and the ground solid sample (the red line, emission wavelength: 568 nm).

Figure 11. Repetitive experiment of mechanochromic behavior for luminogen 4.
compound 1 as an example, as evident from Figure 14, the diffraction curve of the as-synthesized sample displayed many intense and sharp reflection peaks, illustrating its crystalline structure. In contrast, the strong and sharp diffraction peaks vanished after grinding the solid sample in a mortar, which implied that the grinding resulted in a crystal-to-amorphous morphology transition. Moreover, upon treatment with dichloromethane solvent vapor, many sharp and intense diffraction peaks reappeared, indicating its crystalline state was restored. Therefore, the powder XRD results suggested that the mechano-fluorochromic behavior for 1 was attributed to the interconversion between crystalline and amorphous states. Similarly, as can be seen in Figures S22–S26 (Supporting Information), the pristine powder of compounds 2–6 also exhibited intense and sharp peaks, indicating their crystalline morphology, and the powder XRD patterns obtained upon grinding did not show any obvious diffraction peaks, indicating the formation of amorphous morphology, and the initial diffraction peaks could be restored after treatment with fuming dichloromethane vapor. Based on the above-mentioned analyses, the mechno-fluorochromic behaviors of 2–6 could also be attributed to the morphology transition between the crystalline and amorphous states. In addition, fortunately, single crystals of 3 were successfully grown by the recrystallization method. The fluorescence quantum yield of these single crystals was 74.87%, and the fluorescence lifetime was 4.80 ns (Figure S27). The corresponding fluorescence spectrum and fluorescence image of these single crystals were shown in Figures S28 and S29 (Supporting Information). Detailed crystal information is provided in the Tables S1 and S2 (Supporting Information). As can be seen in Figure 15, the molecular conformation of compound 3 is twisted due to the existence of tetraphenylethene unit. Indeed, the twisted molecular conformation and the presence of weak intermolecular C−H⋯O ($d_{C−H⋯O} = 2.695$ Å) and C−H⋯π ($d_{C−H⋯π} = 2.207$ Å) interactions lead to a loose packing motif, which may readily collapse upon exposure to mechanical stimuli. As a consequence, the amorphous state is formed, and the blue-green fluorescence was changed to green.

**CONCLUSIONS**

In summary, we developed six highly solid-emissive 1,8-naphthalimide-based compounds. Interestingly, compounds 1–3 showed AIEE characteristics involving fluorescent color change from weak orange to strong green, and compounds 4–6 showed aggregate fluorescence change feature involving fluorescent color change from orange to yellow. Furthermore, these aggregation-induced green light-emitting or aggregation-induced yellow light-emitting luminophors also exhibited different mechno-fluorochromism phenomena. Among them, 1–3 exhibited mechno-fluorochromic phenomena with color changes between blue or blue-green and green emissions, and 4–6 exhibited mechno-chromic characteristics involving fluorescent color change from yellow-green or yellow to yellow or orange. Indeed, 2 and 6 are promising candidates of rewritable recording mediums. According to powder XRD and X-ray single-crystal analyses results, their significative mecha-
not fluorochromic properties should be caused by the morphology transformation and the alteration of molecular packing. This research work provides valuable reference for the rational design of novel 1,8-naphthalimide-based high-contrast mechanochromic fluorescence materials.

■ EXPERIMENTAL SECTION

General Methods. All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. All starting materials and reagents were obtained as analytical grade from commercial suppliers and used without further purification. Compound 1-1,46 compound 1-2,46 compound 1-3,46 compound 1-4,57 and Compound 1-548 were prepared by procedures described in the corresponding literatures. 1H NMR (400 MHz) and 13C NMR (100 or 125 MHz) spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz) and Bruker NMR (100 or 125 MHz) spectrometers. Fluorescence spectra were recorded on a SU ABSOLUTE PL QUANTUM YIELD SPECTROMETER APEX DUO CCD system. The DMF−water mixtures with various water fractions were prepared by tardily adding various water fractions into the DMF solution of samples. The absorption spectra were measured on an Agilent 8453 UV/vis spectrophotometer. XRD studies were recorded on a Shimadzu XRD-6000 diffractometer using Ni-filtered and graphite-monochromated Cu Kα radiation (λ = 1.54 Å, 40 kV, 30 mA). The X-ray crystal-structure determination of compound 3 was obtained on a Bruker APEX CCD system. The DMF−water mixtures with various water fractions were prepared by tardily adding ultrapure water into the DMF solution of samples. The aggregate behaviors of compounds 1−6 were investigated by NanoBrook 90Plus (Brookhaven Instruments). Absolute luminescence quantum yields were measured by HAMAMATSU ABSOLUTE PL QUANTUM YIELD SPECTROMETER C11347. Fluorescence lifetimes were measured by FLS 1000. Column chromatographic separations were carried out on silica gel (200−300 mesh). TLC was performed by using commercially prepared 100−400 mesh silica gel plates (GF254) and visualization was effected at 254 nm.

Crystallographic Details. Single crystals of compound 3 suitable for X-ray analysis were obtained by slow diffusion of n-hexane into a solution of dichloromethane. A crystal of 3 with appropriate dimensions was mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature. The structure was solved by a combination of direct methods (SHELXS−97)59 and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97).60 All non−H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC 1812957 (compound 3).

General Procedure for the Synthesis of Compound 1. A mixture of compounds 1−4 (2.1 mmol, 0.79 g), 1−1 (2.0 mmol, 0.61 g), K2CO3 (3.62 mmol, 0.50 g), and Pd(PPh3)4 (0.087 mmol, 0.1 g) were stirred in toluene (50 mL), and H2O (5 mL) for 16 h under an argon atmosphere at 80 °C. After completion of present reaction, the mixture was extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with brine, dried (Na2SO4), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected yellow-green solid product in a yield of 78%. 1H NMR (400 MHz, CD2Cl2): δ (ppm) 8.49−8.47 (m, 2H), 8.11−8.08 (m, 1H), 7.62−7.56 (m, 2H), 7.19−7.17 (m, 2H), 7.13−7.11 (m, 2H), 7.10−6.98 (m, 15H), 4.15−4.09 (m, 2H), 1.22 (t, J = 6 Hz, 3H). 13C NMR (100 MHz, CD2Cl2): δ (ppm) 164.4, 164.2, 147.0, 144.6, 144.1, 143.9, 142.4, 140.9, 137.3, 132.9, 131.9, 131.7, 131.6, 131.2, 130.9, 130.5, 129.7, 129.1, 128.2, 127.2, 127.1, 127.0, 123.5, 122.3, 35.8, 13.5. EI-MS: m/z = 555.5 [M]+. Anal. Calcd. for C40H29NO2: C, 86.55; H, 5.33; N, 2.47.

General Procedure for the Synthesis of Compound 2. A mixture of compounds 1−4 (2.1 mmol, 0.79 g), 1−2 (2.0 mmol, 0.64 g), K2CO3 (3.62 mmol, 0.50 g), and Pd(PPh3)4 (0.087 mmol, 0.1 g) were stirred in toluene (50 mL), and H2O (5 mL) for 16 h under an argon atmosphere at 80 °C. After completion of present reaction, the mixture was extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with brine, dried (Na2SO4), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected white solid product in a yield of 75%. 1H NMR (400 MHz, CD2Cl2): δ (ppm) 8.49−8.45 (m, 2H), 8.10−8.07 (m, 1H), 7.60−7.55 (m, 2H), 7.18−7.16 (m, 2H), 7.13−7.10 (m, 2H), 7.09−6.98 (m, 15H), 4.04−4.00 (m, 2H), 1.70−1.61 (m, 2H), 0.91 (t, J = 8 Hz, 3H). 13C NMR (100 MHz, CD2Cl2): δ (ppm) 164.6, 164.4, 146.9, 146.4, 144.1, 144.0, 143.9, 142.4, 140.9, 139.3, 132.8, 131.9, 131.7, 131.6, 131.2, 130.9, 130.5, 129.7, 129.1, 128.2, 128.2, 127.1, 127.1, 127.1, 127.1, 123.5, 122.3, 42.3, 21.8, 11.8. EI-MS: m/z = 569.5 [M]+. Anal. Calcd. for C42H33NO2: C, 86.44; H, 5.48; N, 2.46. Found: C, 86.40; H, 5.41; N, 2.51.

General Procedure for the Synthesis of Compound 3. A mixture of compounds 1−4 (2.1 mmol, 0.79 g), 1−3 (2.0 mmol, 0.66 g), K2CO3 (3.62 mmol, 0.50 g), and Pd(PPh3)4 (0.087 mmol, 0.1 g) were stirred in toluene (50 mL), and ethanol (50 mL), and H2O (5 mL) for 16 h under an argon atmosphere at 80 °C. After completion of present reaction, the mixture was extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with brine, dried (Na2SO4), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected yellow-green solid product in a yield of 79%. 1H NMR (400 MHz, CD2Cl2): δ (ppm) 8.49−8.47 (m, 2H), 8.10 (d, J = 12 Hz, 1H), 7.62−7.56 (m, 2H), 7.18 (d, J = 8 Hz, 2H), 7.12 (d, J = 8 Hz, 2H), 7.09−6.98 (m, 15H), 4.07 (d, J = 6 Hz, 2H), 1.63−1.58 (m, 2H), 1.38−1.30 (m, 2H), 0.89 (t, J = 8 Hz, 3H). 13C NMR (100 MHz, CD2Cl2): δ (ppm) 164.6, 164.4, 146.9, 144.6, 144.1, 144.0, 143.9, 142.4, 140.9, 137.3, 132.8, 131.9, 131.7, 131.6, 131.2, 130.9, 130.5, 129.7, 129.1, 128.2, 127.1, 127.1, 127.0, 123.5, 122.3, 40.5, 30.7, 20.8, 14.1. EI-MS: m/z = 583.5 [M]+. Anal. Calcd. for C44H31NO2: C, 86.42; H, 5.70; N, 2.40. Found: C, 86.35; H, 5.74; N, 2.35.

General Procedure for the Synthesis of Compound 4. To a deoxygenated mixture of compounds 1−1 (5.6 mmol, 1.7 g), 1−5 (6.1 mmol, 2.2 g), Pd(OAc)2 (0.4 mmol, 90 mg),
To a deoxygenated mixture of compounds 1-2 (5.6 mmol, 1.78 g, 1-5 (6.1 mmol, 2.2 g), Pd(OAc)$_2$ (0.4 mmol, 90 mg), K$_2$CO$_3$ (6.8 mmol, 0.94 g), and tetra-n-butylammonium bromide (6.6 mmol, 2.13 g), was added anhydrous DMF (100 mL). The reaction mixture was stirred at 110 °C for 18 h. After completion of present reaction, the mixture was extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected yellow solid product in a yield of 62%. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ (ppm) 8.50–8.45 (m, 3H), 7.90 (d, $J = 8$ Hz, 1H), 7.78 (d, $J = 16$ Hz, 1H), 7.70 (t, $J = 7$ Hz, 1H), 7.35 (d, $J = 8$ Hz, 2H), 7.21 (t, $J = 16$ Hz, 1H), 7.09–6.95 (m, 17H), 4.15–4.09 (m, 2H), 1.22 (t, $J = 8$ Hz, 3H).

$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): δ (ppm) 164.5, 145.0, 144.1, 144.0, 143.0, 153.2, 152.2, 131.7, 131.6, 131.3, 131.1, 130.2, 129.9, 128.7, 128.1, 128.0, 127.0, 127.0, 126.9, 126.9, 124.1, 123.7, 123.6, 122.0, 35.7, 13.5. EI-MS: $m/z = 581.5$ [M$^+$].

Analog. Calcld. for C$_{32}$H$_{23}$NO$_2$: C, 86.72; H, 5.37; N, 2.41.

Found: C, 86.75; H, 5.85; N, 2.23.

**ASSOCIATED CONTENT**

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02110.

NMR spectra; mass spectra; UV–vis absorption spectra of compounds 1–6 (concentration: 20 μM) in DMF–water mixtures with different volume fractions of water (0–90%); decay curves (excitation wavelength: 365 nm) of luminogens 2, 3, 5, and 6 in various solid states; repetitive experiment of mechanochromic behaviors for luminogens 2, 3, 5, and 6; powder XRD patterns of compounds 2–6 in various solid states

Detailed crystal information of luminogen 3 (CIF)

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**Notes**

The authors declare no competing financial interest.

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