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Circularly Polarized Fluorescence Resonance Energy Transfer (C-FRET) for Efficient Chirality Transmission within an Intermolecular System

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Abstract: The occurrence and transmission of chirality is a fascinating characteristic of nature. However, the intermolecular transmission efficiency of circularly polarized luminescence (CPL) remains challenging due to the poor through-space energy transfer. Here we report a unique CPL transmission from inducing the achiral acceptor to emit CPL within a specific liquid crystal (LC)-based intermolecular system through a circularly polarized fluorescence resonance energy transfer (C-FRET), wherein the luminescent cholesteric LC is employed as the chirality donor, and rationally designed achiral long-wavelength aggregation-induced emission (AIE) fluorophore act as the well-assembled acceptor. In contrast to photon-release-and-absorption, the chirality transmission channel of C-FRET is highly dependent upon the energy resonance in the highly intrinsic chiral assembly of cholesteric LC, as verified by deliberately separating the achiral acceptor from the chiral donor to keep far beyond the resonance distance. This C-FRET mode provides a de novo strategy concept for high-level information processing for applications such as high-density data storage, combinatorial logic calculation, and multilevel data encryption and decryption.

Introduction

The occurrence and transmission of chirality is an essential feature of nature,^[1] and plays an important role in biological evolutions,^[2] asymmetric catalysis,^[3] and chiral materials.^[4] Generally, chirality transmission can be classified into two types: intramolecular modes and intermolecular modes. In chiral functional materials, the intermolecular chirality transmission is

most fascinating but the efficiency remains limited due to its through-space energy transfer pathway.^[1c,5a] Until now, improving the intermolecular chirality transmission efficiency has proved highly challenging,^[5b] and considered as the bottleneck especially in the transmission of circularly polarized luminescence (CPL). Generally, CPL exhibits left- or right-handed fluorescence, which can be regarded as part of a high-level visual perception for supplying one more dimension information than regular fluorescence. Chiroptical functional materials with CPL are attracting increasing interest in photonic technologies, such as 3D optical imaging,^[6] chiral sensors,^[7] and photoelectric devices.^[8] Accordingly, there are major opportunities to circumvent this bottleneck of intermolecular CPL transmission, and this field urgently requires a straightforward and general route to efficient chirality transmission.

Given the highly intrinsic chiral assembly of the cholesteric liquid crystals (LCs),^[9] we incorporated a cholesteric unit to construct a specific aggregation-induced emission (AIE) tetraphenylethene (TPE)-based LC as the energy/chirality donor with a chiral scaffold, along with an achiral long-wavelength AIE fluorophore with flexible alkyl chains as the well-assembled acceptor. Through the non-radiative energy transfer from the chiral donor, the achiral acceptor could emit bright CPL with efficient transmission, achieving both chirality transmission and fluorescence resonance energy transfer (FRET) within this intermolecular system (Figure 1). This chirality transmission channel is critically dependent upon the highly ordered cholesteric LC state, which can be attributed to the unique circularly polarized fluorescence resonance energy transfer (C-FRET) rather than the photon-release-and-absorption. In the highly efficient

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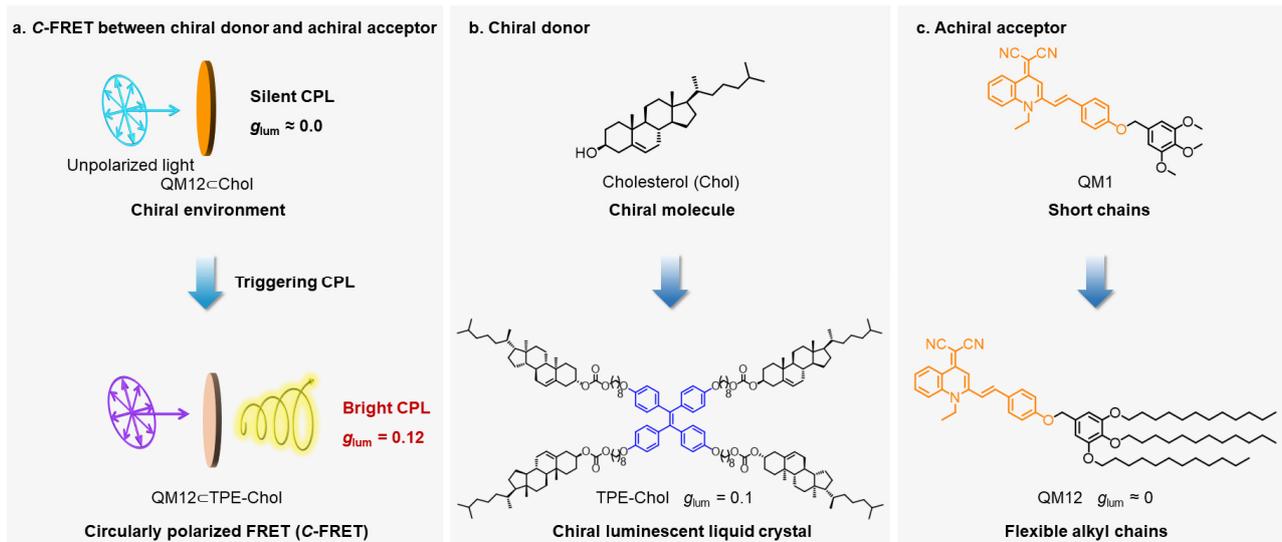


Figure 1. Circularly polarized fluorescence resonance energy transfer (C-FRET) between chiral donor and achiral acceptor. (a) Schematic CPL representation of TPE-Chol and QM12<TPE-Chol. Rational design of (b) chiral TPE-Chol based on chiral liquid crystal cholesterol and (c) achiral QM12 based on the AIEgen building block of quinoline-malononitrile (QM). When orange-emitting AIEgen QM12 dissolved into cholesterol forming QM12<Chol, QM12 emits silent CPL excited directly by regular 460 nm light. And when QM12 dissolved into CPL donor TPE-Chol forming C-FRET system QM12<TPE-Chol, acceptor QM12 emits bright CPL excited indirectly by 330 nm regular light.

intermolecular CPL transmission from chiral donor to achiral acceptor, the C-FRET was verified by deliberately separating the acceptor from the CPL-active donor to it keep far beyond the resonance distance. By virtue of this strategy, the cholesteric-based co-assembly intermolecular system can realize an efficient C-FRET channel with chirality amplification, and simultaneously achieve a high luminescent dissymmetry of CPL ($g_{lum} = 0.12$) and strong emission efficiency (42.8%), thereby successfully building high-density information capacities and anti-counterfeiting technologies.

Results and Discussion

Molecular engineering on chiral LC donor and achiral acceptor

The luminescent dissymmetry and emission efficiency are the two most critical indexes for CPL-active materials.^[10] Generally, in the pursuit of high dissymmetry process, the emission efficiency was suppressed unwarily.^[11] Here, we make full use of the “step-by-step” strategy to construct a CPL-active material with both a high dissymmetry factor and strong emission (Figure 1b). Cholesteric LC was selected as the chiral matrix being capable of self-organizing into helical superstructures with observable helical pitch and high dissymmetry. To avoid aggregation-caused quenching (ACQ) disadvantages in the condensed state, we incorporated an AIE luminogen (AIEgen)^[12] of tetraphenylethylene (TPE) into cholesterols as the chiral donor (TPE-Chol). Other kinds of AIE-active quinoline-malononitrile (QM) derivatives^[13] were also designed as the fluorescence acceptor by consideration of the spectral overlap between energy donor emission and acceptor absorption. We attached three long alkyl chains into QM12 to enhance both the miscibility and co-assembly of the flexible liquid crystal (Figure 1c), focusing on addressing the major dilemma between high dissymmetry and

strong emission within the intermolecular system of chiral donor TPE-Chol and achiral QM acceptor.

Enhancing the miscibility of LC-based co-assembly to improve energy transfer

Fast directional transfer of excitation energy within the chromophore assemblies is crucial to the energy transfer processes such as organogel-dependent white light modulation between functional dyes and π -conjugated systems.^[14] Given the self-organized helical superstructures with one-dimensionally intrinsic long-range orientational order,^[9a,10] the nematic cholesteric LCs can be considered as an ideal matrix for efficient energy transfer and chirality transmission. Figure 2a shows the differential scanning calorimetry thermograms (DSC) of TPE-Chol measured on heating and cooling at a rate of 5 °C min⁻¹, two exothermic transitions at 105 and 78 °C, along with a glass transition at around 32 °C were detected during cooling. The onset temperature of two transitions during cooling was comparable to that during heating, and the transition temperature during cooling was independent upon the cooling rate (Figure S1). These results indicate that the two transitions are associated with LC transition, that is, TPE-Chol formed two LC phases when the temperature was increased higher than glass transition temperature (Figure 2a).^[15] As shown in the polarizing optical microscope (POM) image of oily-streak texture snapshot at 96 °C (Figure 2b), TPE-Chol was directly identified as a typical chiral liquid crystal.^[16] Both DSC and POM results indicate that the cholesteric LC system of TPE-Chol can provide an intrinsically ordered assembly environment to take insight into the energy transfer and chirality transmission.

Beyond the chiral liquid crystallinity, TPE-Chol possesses a typical AIE nature, along with emitting strong cyan fluorescence under UV light irradiation with a high fluorescence quantum yield (QY) of 72.3% ($\lambda_{ex} = 330$ nm) in the solid film state (Figures 2c, S5 and S6). Given a chiral luminescent donor for energy transfer,

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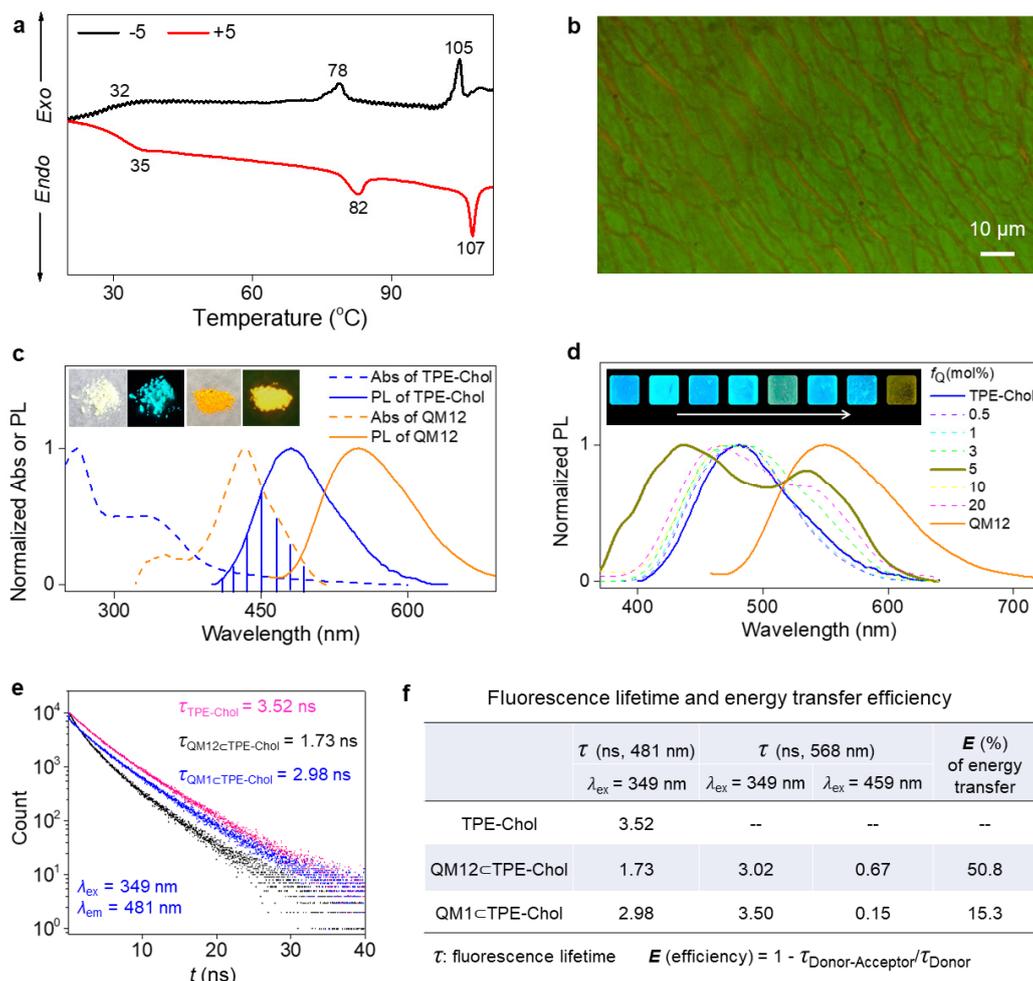


Figure 2. Intermolecular energy transfer in liquid crystal. (a) DSC heating and cooling curves of typical liquid crystal TPE-Chol at a rate of 5 °C min⁻¹. (b) POM image of TPE-Chol snapshotted at 96 °C showing oily streaks texture, indicative of a typical chiral texture of liquid crystal. (c) Normalized absorption (dashed line) and emission (solid line) spectra of TPE-Chol (blue, $\lambda_{ex} = 330$ nm) and QM12 (orange, $\lambda_{ex} = 440$ nm) in solid-state. Inset: photographs of TPE-Chol and QM12 under daylight and UV light, respectively. (d) Fluorescence spectral changes of TPE-Chol in thin film with different molar ratio of QM12 (f_Q): $\lambda_{ex} = 330$ nm except for QM12 ($\lambda_{ex} = 440$ nm), 25 °C. Inset: Fluorescence images of TPE-Chol, and 0.5%, 1%, 3%, 5%, 10%, 20% molar ratio of QM12<TPE-Chol, as well as QM12. (e-f) Fluorescence decay and energy transfer efficiency of TPE-Chol, QM12<TPE-Chol (QM12/TPE-Chol = 5% molar ratio), and QM1<TPE-Chol (QM1/TPE-Chol = 5% molar ratio) in thin film state.

the challenge is to identify a suitable acceptor for trapping the excitation energy through an ordered co-assembly system. For improving the miscibility and co-assembly of flexible liquid crystal, another AIEgen QM12 substituted with three long alkyl chains (Figures S7 and S8) was exploited as the acceptor within the LC scaffold of TPE-Chol (QM12<TPE-Chol) for the sake of the efficient energy transfer. To our knowledge, this is the first use of dual-AIE mode (QM12<TPE-Chol), exhibiting highly emissive in the condensed state without aggregation caused quenching effect, which is desirable for enhancing the efficient energy transfer.^[17]

Figure 2c shows normalized absorption and emission spectra of TPE-Chol and QM12 in the solid state. QM12 exhibits a broad absorption band from 325 to 520 nm, which well overlaps with the fluorescence band of TPE-Chol from 400 to 520 nm. By gradually encapsulating QM12 within TPE-Chol upon excitation at 330 nm, the fluorescence spectra of QM12<TPE-Chol were slightly broadened with the increase in the molar fraction of QM12 (f_Q) from 0% to 3% (Figure 2d). When increasing the f_Q to 5%, a new emission wavelength was presented at 530 nm with around 60

nm redshift, which showed a characteristic fluorescence from QM12, indicative of a possible intermolecular energy transfer.^[18] Conversely, when f_Q was increased to 20%, the emission intensity became dropped obviously at 530 nm. This result might be attributed that the liquid crystallinity of TPE-Chol was destroyed when redundantly adding high amount of QM12, thereby distinctly weakening the intermolecular energy transfer. Here the doping concentration at 5% was an appropriate ratio, along with a fluorescence quantum yield of 42.8%, since the fluorescence energy of the donor could be effectively transferred to the acceptor.

Except for QM12<TPE-Chol, another co-assembly mode QM1<TPE-Chol was employed as a reference to investigate the energy transfer efficiency. We carried out the fluorescent lifetime test to evaluate the energy transfer efficiency of QM12<TPE-Chol and QM1<TPE-Chol both at the doping fraction (f_Q) of 5% (Figures 2e-f, S11 and S12). Their fluorescence lifetimes (568 nm), monitored at the acceptor emission (QM12 and QM1), were both extended from direct excitation (459 nm) to indirect excitation

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(349 nm), which is in agreement with the energy transfer mechanism.^[19] The transfer efficiency is typically measured using the relative fluorescence lifetime (τ) of the donor, in the absence (Donor) and presence (Donor-Acceptor) of acceptor: E (efficiency) = $1 - \tau_{\text{Donor-Acceptor}}/\tau_{\text{Donor}}$, which is applicable to donor-acceptor pairs that are separated by a fixed distance. As shown in Figure 2e, while excited by 349 nm light, the lifetime of TPE-Chol ($\tau_{\text{TPE-Chol}} = 3.52$ ns) was measured at 481 nm. Meanwhile, we observed a decreased donor fluorescence lifetime ($\tau_{\text{QM12}\subset\text{TPE-Chol}} = 1.73$ ns) in the co-assembly mode of QM12 \subset TPE-Chol. Thus, the energy transfer efficiency was calculated as 50.8%, indicative of the highly efficient energy transfer from TPE-Chol to QM12. In contrast, the reference system of QM1 \subset TPE-Chol showed a much less energy transfer (15.3%). Compared with QM1 \subset TPE-Chol, the additional three grafted long alkyl chains of QM12 can indeed increase the energy transfer efficiency in the intermolecular co-assembly, which might result from the matchable co-assembled system in QM12 \subset TPE-Chol with the enhanced miscibility between the flexible alky chain-based QM12 and TPE-Chol.

Efficient chirality transmission in chiral-LC-based co-assembly

Beyond energy transfer, the chirality transmission could occur synchronously in the encapsulation of QM12 \subset TPE-Chol. Since TPE-Chol possesses a typical chiral LC nature, we employed a popular method, CPL, to investigate the chirality transfer of TPE-Chol and QM12 \subset TPE-Chol. Compared with the CD test (Figure S16), CPL can be used to evaluate the macroscopic chirality of chiral fluorescence dyes in the excited state. The primary criterion for appraising CPL is to measure luminescence dissymmetry factor, $g_{\text{lum}} = 2(I_{\text{L}} - I_{\text{R}})/(I_{\text{L}} + I_{\text{R}})$, which provides the excited-state luminescence difference of left (L) and right (R) circularly polarized light.^[20] For CPL, a high g_{lum} value is an important standard to evaluate the chiroptical property. As shown in Figure 3a and 3e, a strongly positive CPL signal of TPE-Chol at 472 nm was observed, and stayed completely consistent with its fluorescence ($\lambda_{\text{em}} = 472$ nm) in the condensed state. After encapsulating QM12 into LC TPE-Chol, the CPL peak of QM12 \subset TPE-Chol shifted from 472 to 545 nm upon indirect excitation at 330 nm (Figure 3e). QM12 \subset TPE-Chol exhibited a positive CPL signal in the fluorescence emission range of QM12, accompanied by the disappearance of the CPL peak of TPE-Chol. Similarly, the maximum g_{lum} peak also shifted from 434 to 570 nm in agreement with CPL, which was also located in the zone of QM12 (Figure S17 and S18). Within the intermolecular LC-doping system, the chirality transmission between chiral donor TPE-Chol and achiral acceptor QM12 was successfully realized in the form

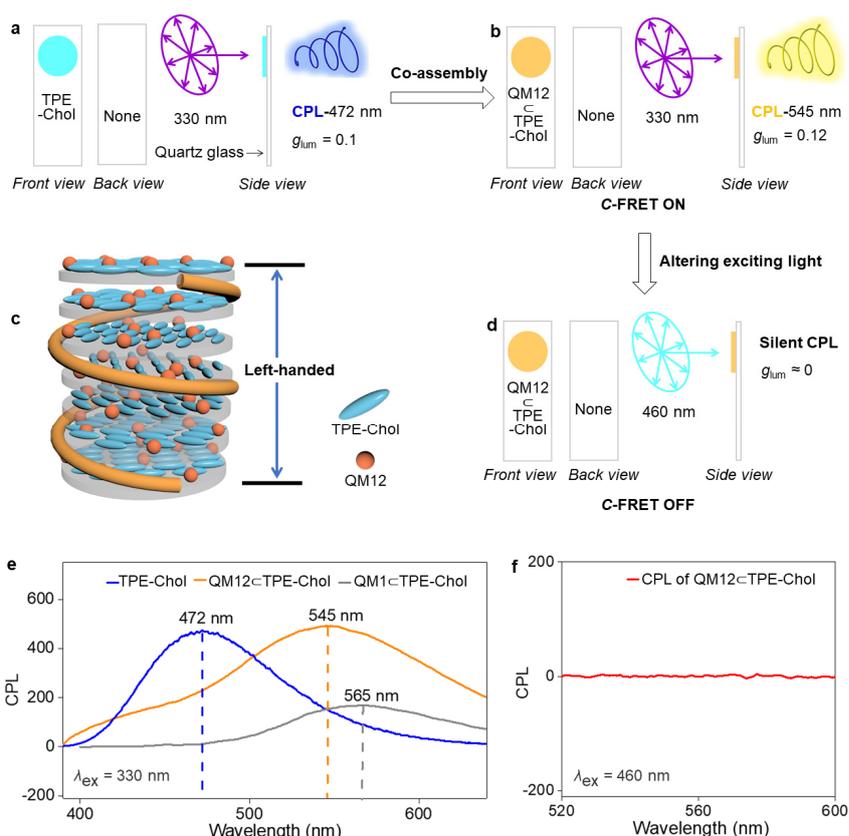


Figure 3. Efficient chirality transmission occurred synchronously in liquid crystal. (a) Schematic CPL representation of TPE-Chol. (b) Chirality transmission and energy transfer of QM12 \subset TPE-Chol. Donor: TPE-Chol (chiral luminescent liquid crystal); Acceptor: QM12 (achiral dye). When co-assembled with the chiral liquid crystal, QM12 could capture the CPL from TPE-Chol and emit CPL; Note: QM12/TPE-Chol = 5% molar ratio. (c) Molecular organization of QM12 \subset TPE-Chol in cholesteric LC phases, according to positive CPL value, the helical superstructure of QM12 \subset TPE-Chol could be left-handed. (d) Altering exciting light from 330 to 460 nm light for QM12 \subset TPE-Chol. (e) Spectral changes of CPL transmission between donor TPE-Chol and acceptor QM12/QM1 (5% molar ratio) excited at 330 nm. (f) CPL spectrum of QM12 \subset TPE-Chol excited at 460 nm; Note: QM12/TPE-Chol = 5% molar ratio.

of fluorescence energy transfer. To rule out the medium-mediated circular polarisation induction, a Bragg reflection test was employed. As shown in Figure S20, the Bragg reflection of TPE-Chol was away from the visible light region, and no reflection color was observed, which strongly ruled out the LC cholesteric stacks and verified the CPL transmission process.

Due to the positive CPL signal, the helical superstructure of QM12 \subset TPE-Chol is considered as left-handed (Figure 3c). For g_{lum} analysis (Figure S17 and S18), the maximally calculated g_{lum} value of TPE-Chol is about 0.1 in the thin film state ($d_{\text{thickness}} = 10$ μm), which is much higher than other reported values (10^{-5} – 10^{-3}).^[20b] Coupled with a high quantum yield of 72.3%, liquid crystal TPE-Chol showed superb chiroptical properties and liquid crystallinities, thereby successfully constructing a brand-new chiral fluorescent LC. Impressively, the maximal g_{lum} value of QM12 \subset TPE-Chol is 0.12, which is even slightly increased from 0.1 of TPE-Chol (Figure S18), indicative of a highly efficient chirality transmission accompanied with energy transfer within the intermolecular co-assembly mode of QM12 \subset TPE-Chol.

As energy transfer, QM1 was employed as a reference to investigate the influence of acceptor structure on CPL transmission. As shown in Figure 3e and S18, although the CPL

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peak of QM12cTPE-Chol shifted from 472 to 565 nm upon indirect excitation at 330 nm, its g_{lum} value at 570 nm (0.03) was only a quarter of QM12cTPE-Chol (0.12). In agreement with the energy transfer, here the efficient chirality transmission is feasible only in the case of the well co-assembled system of QM12cTPE-Chol, which was further certified by the CD behavior of QM12cTPE-Chol and QM1cTPE-Chol (Figure S21 and S22). Considering these results together, we have successfully developed a generalizable strategy—a pair of chiral donor and well-assembled achiral acceptor—for improving the intermolecular chirality transfer efficiency.

To further confirm the high g_{lum} value of QM12cTPE-Chol results from the fluorophore-fluorophore intermolecular interaction rather than its chiral environment, we also measured the g_{lum} upon direct excitation and indirect excitation. As mentioned above, QM12 showed obvious absorbance at 460 nm, while TPE-Chol had non-absorbance in this region. In this case, we excited QM12cTPE-Chol at 460 nm (*i. e.* directly excited QM12 in chiral environment), and nearly zero CPL was detected (Figure 3f). Accordingly, the observed dissymmetry factor $|g_{lum}|$ of QM12cTPE-Chol by the indirect excitation at 330 nm (0.12) is much larger than the one by the direct excitation at 460 nm. This super gap demonstrates that the efficient chirality transmission and amplification could occur synchronously by indirect excitation ($\lambda_{ex} = 330$ nm) within the intermolecular system of QM12cTPE-Chol.

C-FRET rather than photon-release-and-absorption

Fluorescence resonance energy transfer (FRET) is one kind of energy transfer, and a heavily studied topic in contemporary chemistry. In FRET, the through-space transfer of energy transfers from an excited donor to an acceptor that subsequently emits this energy as light. As mentioned above, the AIEgen fluorescence lifetime of the donor (Figure 2e and 2f) became shortened from free donor TPE-Chol (3.52 ns) to the highly intrinsic chiral assembly of QM12cTPE-Chol (1.73 ns), indicating that there occurred a possible FRET process upon indirect excitation from TPE-Chol within the intermolecular co-assembly system. It is the highly ordered chiral assembly of the cholesteric LC system that we have successfully constructed a specific LC-based intermolecular system, and achieved an efficient CPL chirality transmission and amplification occurred synchronously during the circularly polarized fluorescence resonance energy transfer (C-FRET).

It is well known that two prerequisites should be satisfied to achieve FRET effect: (i) a good overlap between the emission spectrum of donor and the absorption spectrum of acceptor; (ii) a proper distance between the donor and the acceptor (< 100 Å).^[18,19] To verify the concept of C-FRET, we attempted to encapsulate QM12 within pure cholesterol without the FRET donor (Figure 4a), that is, QM12cChol exhibited nearly zero CPL. As illustrated with a phase-separated trial of TPE-Chol→QM12

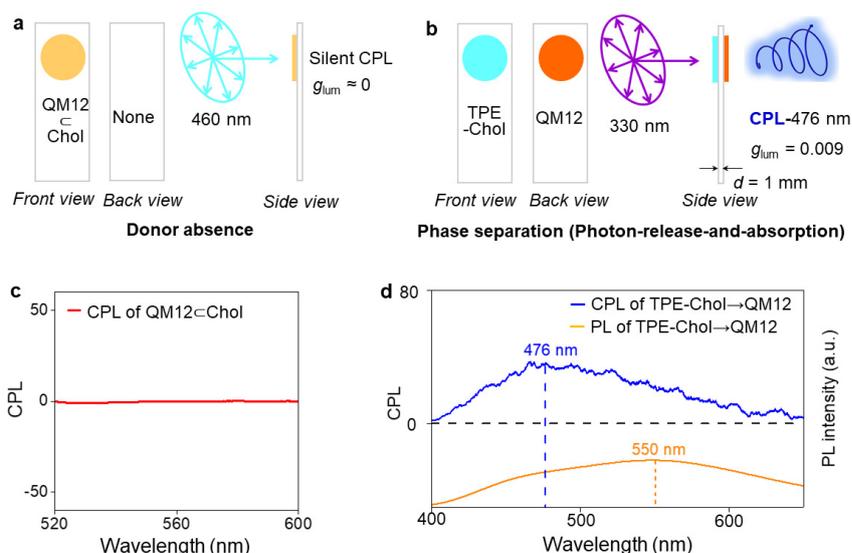


Figure 4. Verifying the concept of C-FRET in the absence of donor or in the phase separation state. (a) Schematic CPL representation of QM12cChol. (b) In the status of phase separation (TPE-Chol→QM12), QM12 was unable to capture CPL but able to capture regular fluorescence from TPE-Chol. (c) CPL and g_{lum} spectra of QM12cChol excited at 460 nm. (d) CPL (d), emission (d), and g_{lum} (e) spectra of TPE-Chol in the presence but separation of QM12 (TPE-Chol→QM12) excited at 330 nm.

(Figure 4b), donor TPE-Chol and acceptor QM12 were coated on two sides of quartz glass, respectively, to maintain a separation between donor and acceptor. Specifically, the thickness of the glass was 1.0 mm, well out of the efficient resonance distance (< 100 Å). According to the array of CPL device (Figure S24), 330 nm excitation light was placed on the side of TPE-Chol, and the CPL and fluorescence spectra of TPE-Chol→QM12 could be simultaneously detected from the side of QM12 simultaneously. We note that the excitation light of CPL or fluorescence in CPL device was horizontal with the direction of signal detection, rather than in the orthogonal direction as in regular fluorescence devices.

As expected, we observed two completely different results on CPL and fluorescence spectra. On the CPL hand, a positive CPL of TPE-Chol→QM12 was found at 476 nm upon 330 nm light irradiation (Figure 4b), which could be ascribed to TPE-Chol. Similar to CPL, the g_{lum} peak of TPE-Chol→QM12 also located in the range of TPE-Chol (Figure S25). Obviously, the chirality of TPE-Chol was not transferred to QM12 in the phase-separated state. On the fluorescence hand, an intensive peak was found at 550 nm resulted from AIEgen QM12 while excited by 330 nm light, indicating that the fluorescence of TPE-Chol could make QM12 emit fluorescence. Given that the distance of TPE-Chol phase and QM12 phase (1.0 mm) was out of the FRET range (< 100 Å), the fluorescence energy transfer of TPE-Chol→QM12 relied on a photon-release-and-absorption mechanism (a radiative energy transfer). In the phase-separated state of TPE-Chol→QM12, we observed no chirality transmission, which was quite distinct from a non-radiative process based on the process of C-FRET. By purposefully separating the acceptor from the LC-active donor to keep it far beyond the resonance distance, we prove the C-FRET concept of QM12cTPE-Chol from the perspective of the key FRET prerequisites. Taking advantage of its strong AIE property, flexible liquid crystallinity and optical chirality, TPE-Chol is expected to be an excellent CPL donor and chiral scaffold to co-assemble with acceptor QM12 into chiral encapsulation modes,

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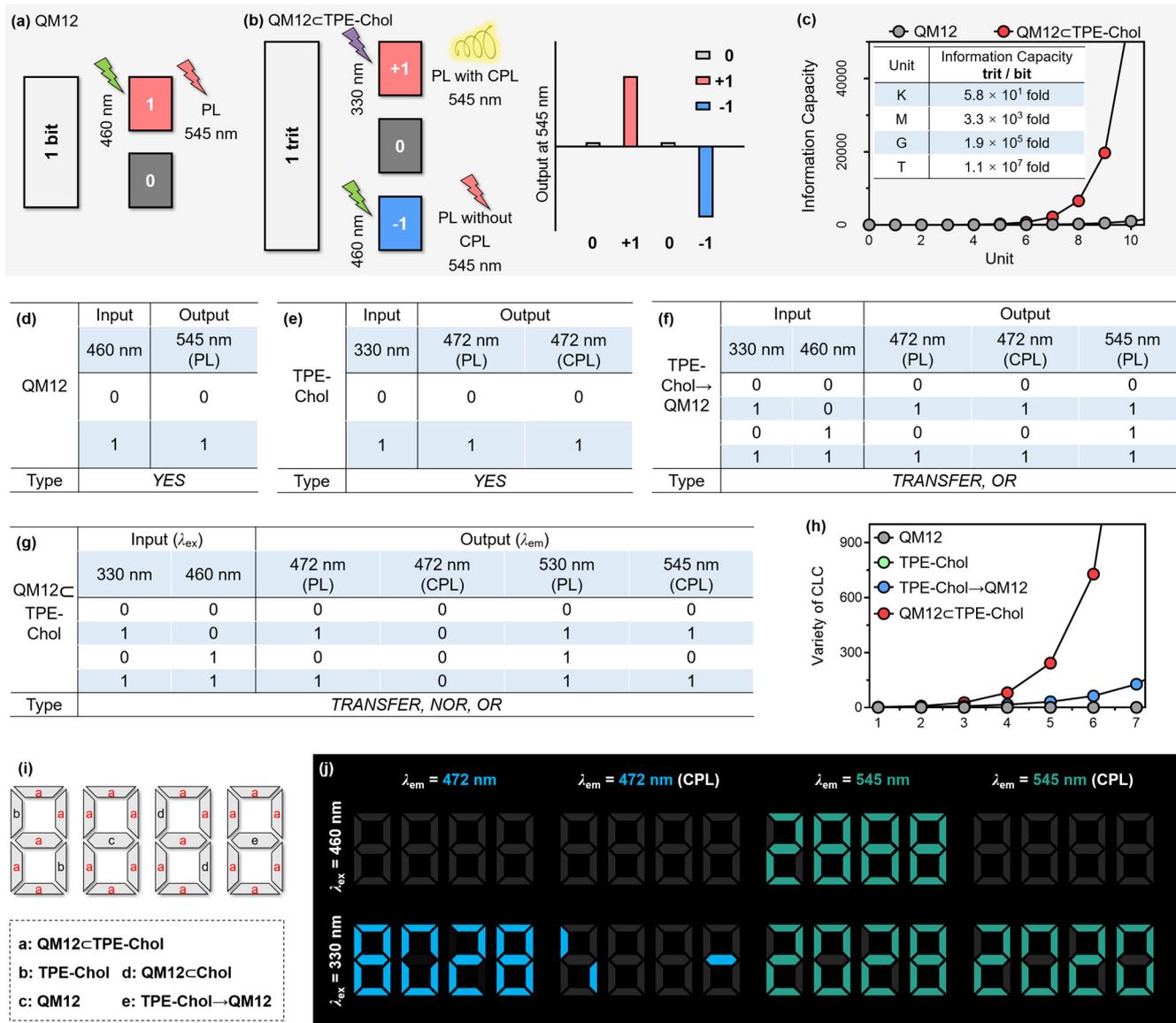


Figure 5. C-FRET enables high-density data storage, combinatorial logic calculation, as well as multilevel data encryption and decryption. (a and b) The outputs of QM12 (binary logic system: “0” and “1”) and QM12cTPE-Chol (ternary logic system: “0”, “+1”, and “-1”) under excitation at 330 or 460 nm. (c) The exponential enhancement of information capacity from QM12 to QM12cTPE-Chol (i.e. from “bit” to “trit”). (d-g) The truth table and logic gate types of QM12, TPE-Chol, TPE-Chol to QM12, and QM12cTPE-Chol. (h) The variety of combinational logic circuit (CLC) in QM12, TPE-Chol, TPE-Chol to QM12, and QM12cTPE-Chol. (i) Pattern designed with different phosphors. (j) Thought experiment: experimental setup for the multilevel anti-counterfeiting device. By modulating the excitation (λ_{ex} = 330 or 460 nm) and output mode, different information at 472 nm (PL and CPL) and 545 nm (PL and CPL) can be recorded.

thus achieving the specific C-FRET with efficient chirality transmission efficiency within an intermolecular system.

Information processing based on C-FRET

It is well known that the information density limits in memory devices could be overcome by moving from a binary (using “bit” as the unit) to a ternary logic system (using “trit” as the unit).^[21] However, for most fluorophores, the inherent characteristics (emit or not) made them impractical in binary systems. For example, the outputs of QM12 (emission at 545 nm) are only “1” (with excitation at 460 nm), and “0” (without excitation at 460 nm) (Figure 5a). Clearly, the information capacity of this binary system is 2^n (“0” or “1” in each unit). In contrast, the chiral inversion in QM12cTPE-Chol allows multiplexing because: (i) when excited at 330 nm, QM12cTPE-Chol emits at 545 nm with CPL (output

“+1”); (ii) when excited at 460 nm, QM12cTPE-Chol emits at 545 nm without CPL (output “-1”); and (iii) without excitation, QM12cTPE-Chol does not emit (output “0”) (Figure 5b). These desirable three outputs (combined “+1”, “0”, and “-1”) are the typical feature of a ternary logic system. This means that the diversity of QM12cTPE-Chol in each unit is 1.5-fold than that of QM12, and its information capacity is 3^n (“+1”, “0”, and “-1” in each unit) (Figure 5c). To gain further understanding of this high-density data storage, we calculated the exponential enhancement of information capacity from binary to a ternary logic system (that is, from “bit” to “trit”): the information capacity values of the ternary system (Mt, Gt, and Tt) were 3.3×10^3 -, 1.9×10^5 -, and 1.1×10^7 -fold higher than the respective binary systems (Mb, Gb, and Tb) (Figure 5c). Hence, the C-FRET strategy might enable the

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evolution from binary to ternary systems, greatly improving information capacities.

The various emission outputs of QM12cTPE-Chol also provide the feasibility for constructing combinational logic circuits (CLC).^[22] As shown in Figure 5d-5f, QM12 and TPE-Chol can only build one kind of logic gate (YES), while TPE-Chol→QM12 can only build two kinds (TRANSFER and OR logic gate), which greatly limits their diversity for constructing CLCs. In QM12cTPE-Chol, if we set excitation at 330 and 460 nm as the double-input, and the PL at 472 nm as the single-output, it can be obtained TRANSFER logic gate. Accordingly, we can also build NOR, OR, and TRANSFER logic gates by setting CPL at 472 nm, PL and CPL at 545 nm as the single-output, respectively (Figure S26 and S27). In this case, using QM12cTPE-Chol as a circuit unit enables the diversified combinatorial logic calculation (Figure 5h).

Furthermore, given the unique C-FRET features of QM12cTPE-Chol with various emission outputs at 472 and 545 nm (Figure 5g), we carried out a conceived display: an anti-counterfeiting pattern^[23] “2020” was fabricated using different phosphors (Figure 5i). The photoactivation results are shown in Figure 5j: (i) Under 460 nm visible-light excitation, the pattern only displayed digital numbers “2888” at 545 nm (PL). (ii) In contrast, under 330 nm UV-light excitation, the luminescent pattern could be converted into “8028” at 472 nm (PL), and meaningless information at 472 nm (CPL). (iii) Under 330 nm UV-light excitation, the pattern displayed digital numbers “2028” at 545 nm (PL). (iv) More interestingly, only when the 330 nm light as the input combining with the CPL at 545 nm as the output mode, the true information could be observed as digital numbers “2020”. These various characteristic outputs enable multilevel data encryption and decryption that is distinct from conventional approaches, as well as high-density data storage.

Conclusion

Given that CPL is a high-level visual perception for supplying one more dimension information than regular fluorescence, here we focused on the major dilemma between high dissymmetry and strong emission, which is particularly relevant for intermolecular systems. Making full use of its strong AIE property, flexible liquid crystallinity, and optical chirality, we have developed TPE-Chol as excellent CPL donor, and co-assembled with achiral AIEgen acceptor QM12 into chiral LC scaffold (QM12cTPE-Chol), and successfully achieved the unique intermolecular C-FRET process with efficient chirality transmission efficiency. Three long alkyl chains were specifically grafted into the achiral acceptor of AIEgen QM12 to improve the miscibility and co-assembly of flexible liquid crystal, thus facilitating the efficient energy transfer. The chiral luminescent LC co-assembly with achiral AIEgen can achieve a superb dissymmetry factor of CPL ($g_{lum} = 0.12$) and strong emission efficiency (42.8%), simultaneously, through a non-radiative C-FRET process. We tactfully separated the acceptor from the LC-active donor to keep far beyond the resonance distance, and found that the photon-release-and-absorption process doesn't allow chirality transmission within the intermolecular system. Here the specific chirality transmission channel is critically dependent on the highly ordered cholesteric LC state, endowing with two essential features: (i) the photon-release-and-absorption modes only results in energy transfer; and (ii) the C-FRET mode can transfer and amplify CPL for both

efficient chirality transmission and energy transfer. This dual-AIE chiral-LC-based co-assembly (QM12cTPE-Chol) is highly desirable for the efficient energy transfer, chirality transmission and amplification due to the beneficial AIE characteristic with strong emission in the condensed phase, which can realize a unique C-FRET channel, along with potential practical application to high-density information capacities and new anti-counterfeiting technologies.

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Keywords: aggregation-induced emission • circularly polarized luminescence • self-assembly • FRET • fluorescence

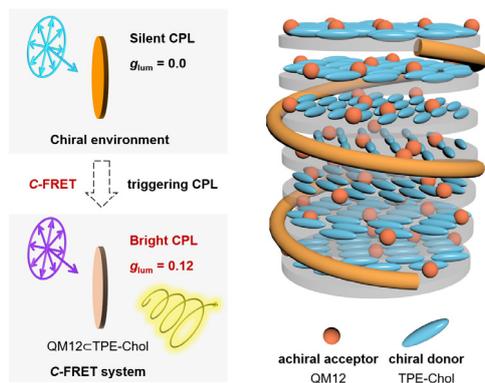
- [1] a) G. H. Wagnière, *On Chirality and the Universal Asymmetry: Reflections on Image and Mirror Image*, John Wiley & Sons, **2008**; b) B. L. Feringa, R. A. Van Delden, *Angew. Chem. Int. Ed.* **1999**, *38*, 3418–3438; *Angew. Chem.* **1999**, *111*, 3624–3645; c) S. M. Morrow, A. J. Bissette, S. P. Fletcher, *Nat. Nanotech.* **2017**, *12*, 410–419.
- [2] a) A. Ceconello, L. V. Besteiro, A. O. Govorov, I. Willner, *Nat. Rev. Mater.* **2017**, *2*, 17039; b) A. Pietropaolo, L. Muccioli, R. Berardi, C. Zannoni, *Proteins* **2008**, *70*, 667–677; c) S. Schoeffner, M. A. Blasco, *Nat. Cell Biol.* **2008**, *10*, 228–235.
- [3] a) R. Noyori, M. Kitamura, *Angew. Chem. Int. Ed.* **1991**, *30*, 49–69; *Angew. Chem.* **1991**, *103*, 34–55; b) S. Shaw, J. D. White, *Chem. Rev.* **2019**, *119*, 9381–9426; J. Mas-Roselló, A. G. Herraiz, B. Audic, A. Laverny, N. Cramer, *Angew. Chem. Int. Ed.* **2021**, *60*, 13198–13224; *Angew. Chem.* **2021**, *133*, 13306–13332.
- [4] a) J. Han, J. You, X. Li, P. Duan, M. Liu, *Adv. Matter.* **2017**, *29*, 1606503; b) L. Xu, C. Wang, Y. X. Li, X. H. Xu, L. Zhou, N. Liu, Z. Q. Wu, *Angew. Chem. Int. Ed.* **2020**, *59*, 16675–16682; *Angew. Chem.* **2020**, *132*, 16818–16825; c) D. P. N. Gonçalves, T. Hegmann, *Angew. Chem. Int. Ed.* **2021**, *60*, 17344–17349; *Angew. Chem.* **2021**, *133*, 17484–17489.
- [5] a) D. L. Andrews, *Methods Appl. Fluoresc.* **2019**, *7*, 032001; b) J. Wade, J. R. Brandt, D. Reger, F. Zinna, K. Y. Amsharov, N. Jux, D. L. Andrews, M. J. Fuchter, *Angew. Chem. Int. Ed.* **2021**, *60*, 222–227; *Angew. Chem.* **2021**, *133*, 224–229; c) D. Yang, P. Duan, L. Zhang, M. Liu, *Nat. Commun.* **2017**, *8*, 15727; d) H. Li, H. Li, W. Wang, Y. Tao, S. Wang, Q. Yang, Y. Jiang, C. Zheng, W. Huang, R. Chen, *Angew. Chem. Int. Ed.* **2020**, *59*, 4756–4762; *Angew. Chem.* **2020**, *132*, 4786–4792; e) Z. Wang, Y. Li, A. Hao, P. Xing, *Angew. Chem. Int. Ed.* **2021**, *60*, 3138–3147; *Angew. Chem.* **2021**, *133*, 3175–3184; f) M. M. Zhang, X. Y. Dong, Z. Y. Wang, H. Y. Li, S. J. Li, X. Zhao, S. Q. Zang, *Angew. Chem. Int. Ed.* **2020**, *59*, 10052–10058; *Angew. Chem.* **2020**, *132*, 10138–10144; g) K. Takaishi, T. Matsumoto, M. Kawataka, T. Ema, *Angew. Chem. Int. Ed.* **2020**, *60*, 9968–9972; *Angew. Chem.* **2020**, *132*, 10056–10060.

RESEARCH ARTICLE

- [6] a) S. Huo, P. Duan, T. Jiao, Q. Peng, M. Liu, *Angew. Chem. Int. Ed.* **2017**, *56*, 12174–12178; *Angew. Chem.* **2017**, *129*, 12342–12346; b) M. Schadt, *Annu. Rev. Mater. Sci.* **1997**, *27*, 305–379; c) H. K. Bisoyi, Q. Li, *Acc. Chem. Res.* **2014**, *47*, 3184–3195.
- [7] a) Y. Yang, R. C. da Costa, M. J. Fuchter, A. J. Campbell, *Nat. Photonics* **2013**, *7*, 634–638; b) K. Hou, J. Zhao, H. Wang, B. Li, K. Li, X. Shi, K. Wan, J. Ai, J. Lv, D. Wang, Q. Huang, H. Wang, Q. Cao, S. Liu, Z. Tang, *Nat. Commun.* **2020**, *11*, 4790; c) D. Li, X. Liu, W. Wu, Y. Peng, S. Zhao, L. Li, M. Hong, J. Luo, *Angew. Chem. Int. Ed.* **2021**, *60*, 8415–8418; *Angew. Chem.* **2021**, *133*, 8496–8499.
- [8] a) X. Zhang, Y. Zhang, H. Zhang, Y. Quan, Y. Li, Y. Cheng, S. Ye, *Org. Lett.* **2019**, *21*, 439–443; b) B. K. An, D. S. Lee, J. S. Lee, Y. S. Park, H. S. Song, S. Y. Park, *J. Am. Chem. Soc.* **2004**, *126*, 10232–10233; c) H. Goto, K. Akagi, *Angew. Chem. Int. Ed.* **2005**, *44*, 4322–4328; *Angew. Chem.* **2005**, *117*, 4396–4402; d) J. W. Canary, *Chem. Soc. Rev.* **2009**, *38*, 747–756.
- [9] a) S. Pieraccini, S. Masiero, A. Ferrarini, G. P. Spada, *Chem. Soc. Rev.* **2011**, *40*, 258–271; b) P. Chen, L. L. Ma, W. Hu, Z. X. Shen, H. K. Bisoyi, S. B. Wu, S. J. Ge, Q. Li, Y. Q. Lu, *Nat. Commun.* **2019**, *10*, 2518; c) Q. Mo, B. Liu, W. Huang, P. Z. Sun, Z. Li, H. K. Bisoyi, D. Shen, Z. G. Zheng, Y. Q. Lu, Q. Li, *Adv. Optical Mater.* **2020**, *8*, 2000155.
- [10] Y. Wu, L. H. You, Z. Q. Yu, J. H. Wang, Z. Meng, Y. Liu, X. S. Li, K. Fu, X. K. Ren, B. Z. Tang, *ACS Mater. Lett.* **2020**, *2*, 505–510.
- [11] T. Zhao, J. Han, X. Jin, Y. Liu, M. Liu, P. Duan, *Angew. Chem. Int. Ed.* **2019**, *58*, 4798–4982; *Angew. Chem.* **2019**, *131*, 5032–5036.
- [12] a) J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* **2015**, *115*, 11718–11940; b) Z. Q. Yu, X. Li, W. Wan, X. S. Li, K. Fu, Y. Wu, A. D. Q. Li, *Chem. Sci.* **2021**, *12*, 3146–3151; c) H. Wu, Z. Chen, W. Chi, A. K. Bindra, L. Gu, C. Qiang, B. Wu, B. Yue, G. Liu, G. Yang, L. L. Zhu, Y. Zhao, *Angew. Chem. Int. Ed.* **2019**, *58*, 11419–11423; *Angew. Chem.* **2019**, *131*, 11541–11545.
- [13] a) Z. Q. Guo, C. X. Yan, W. H. Zhu, *Angew. Chem. Int. Ed.*, **2020**, *59*, 9812–9825; *Angew. Chem.* **2020**, *32*, 9896–9909; b) C. Yan, Z. Guo, J. Zhang, H. Zhang, H. Tian, W. H. Zhu, *J. Am. Chem. Soc.* **2019**, *141*, 3171–3177; c) Y. Wu, P. Jin, K. Gu, C. Shi, Z. Guo, Z. Q. Yu, W. H. Zhu, *Chem. Commun.* **2019**, *55*, 4087–4090; d) J. Y. Yang, Z. G. Chi, W. H. Zhu, B. Z. Tang, Z. Li, *Sci. China Chem.*, **2019**, *62*, 1090–1098.
- [14] A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, S. J. George, *Angew. Chem. Int. Ed.* **2007**, *46*, 6260–6265; *Angew. Chem.* **2007**, *119*, 6376–6381.
- [15] S. Z. D. Cheng, Chapter 4: Metastable states in phase transitions of polymers. *Phase Transitions in Polymers*. Elsevier, **2008**.
- [16] I. Dierking, *Textures of Liquid Crystals*. Wiley-VCH: Weinheim, **2003**.
- [17] B. K. An, D. S. Lee, J. S. Lee, Park, Y. S.; Song, H. S.; Park, S. Y. *J. Am. Chem. Soc.* **2004**, *126*, 10232–10233.
- [18] a) V. K. Praveen, S. J. George, R. Vaghese, C. Vijayakumar, A. Ajayaghosh, *J. Am. Chem. Soc.* **2006**, *128*, 7542–7550; b) A. E. Cohen, S. Mukamel, *J. Phys. Chem. A* **2003**, *107*, 3633–3638; c) J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd ed, Springer US, **2006**.
- [19] R. M. Clegg. Chapter 1: Förster resonance energy transfer—FRET what is it, why do it, and how it's done. *Laboratory Techniques in Biochemistry and Molecular Biology*. Elsevier, **2009**, 33.
- [20] a) J. Kumar, T. Nakashima, T. Kawai, *J. Phys. Chem. Lett.* **2015**, *6*, 3445–3452; b) X. Li, Y. Xie, Z. Li, *Adv. Photonics Res.* **2021**, *2*, 2000136.
- [21] a) J. W. Jeong, Y. E. Choi, W. S. Kim, J. H. Park, S. Kim, S. Shin, K. Lee, J. Chang, S. J. Kim, K. R. Kim, *Nat. Electronics* **2019**, *2*, 307–312; b) K. C. Smith, *IEEE Trans. Comput.* **1981**, C-30, 619–634; c) Y. Wu, Z. Guo, W. H. Zhu, W. Wan, J. Zhang, W. Li, X. Li, H. Tian, A. D. Q. Li, *Mater. Horiz.* **2016**, *3*, 124–129.
- [22] a) A. P. de Silva, N. H. Q. Gunaratne, C. P. McCoy, *Nature* **1993**, *364*, 42–44.
- [23] a) S. Xu, R. Chen, C. Zheng, W. Huang, *Adv. Mater.* **2016**, *28*, 9920–9940; b) L. Gu, H. Shi, M. Gu, K. Ling, H. Ma, S. Cai, L. Song, C. Ma, H. Li, G. Xing, X. Huang, J. Li, Y. Gao, W. Yao, Z. Shuai, Z. An, X. Liu, W. Huang, *Angew. Chem. Int. Ed.* **2018**, *57*, 8425–8431; *Angew. Chem.* **2018**, *130*, 8561–8567.

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Improving the intermolecular transmission efficiency of circularly polarized luminescence (CPL) remains challenging. A unique CPL transmission with circularly polarized fluorescence resonance energy transfer (C-FRET) is verified, along with a high dissymmetry factor and strong emission. This C-FRET mode provides a de novo strategy concept for high-level information processing for applications such as high-density data storage, combinatorial logic calculation, and multilevel data encryption and decryption.