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Fabrication of Ultralong-lived Phosphorescent Materials via Förster Resonance Energy Transfer

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Abstract. Photosynthetic organisms in nature achieve directional transmission and conversion of solar energy via sophisticated light-harvesting complexes, a process closely associated with Förster resonance energy transfer (FRET). When focusing solely on individual photons capable of exciting chlorophyll molecules, the maximum energy transfer efficiency can reach approximately 95%. Inspired by this, numerous artificial-light-harvesting systems (ALHSs) based on cascaded FRET have been developed. Nevertheless, only a handful of examples realize an overall energy transfer efficiency exceeding 80%. Among them, ALHSs with near-infrared phosphorescent emission exhibit distinctive properties, including low toxicity, large Stokes shifts and tunable phosphorescence, and thus have been widely applied in information encryption, bioimaging, materials science and other fields. Fundamentally, the development of near-infrared emissive ALHSs requires lowering the energy level of the molecular triplet excited state (T1). But this change makes non-radiative transitions more likely, so the brightness and duration of phosphorescence both go down. Besides, the energy difference between S1 and T1 becomes much bigger. This slows down intersystem crossing, which also weakens phosphorescence. We thus need new ways to get efficient energy transfer and near-infrared phosphorescence from organic dyes.

Keywords: Förster resonance energy transfer, artificial light-harvesting systems, phosphorescence

1. Introduction

Förster resonance energy transfer (FRET) is a nonradiative energy-transfer process that occurs between two fluorescent molecules or chromophores (figure 1a). The idea was first put forward theoretically in the 1940s by German scientist Theodor Förster, and the effect was later named after him, as displayed in Figure 1b [1]. Since FRET responds strongly to how far and how molecules face each other, researchers widely use this technique to study interactions between molecules in biology and chemical analysis fields.

Förster resonance energy transfer (FRET) is a nonradiative process in which excitation energy is transferred from a donor chromophore to an acceptor through long-range dipole–dipole interactions. Efficient FRET relies on three fundamental requirements [2] (Figure 1c): (i) the donor and acceptor must be separated by only a few nanometers, typically within 1–10 nm; (ii) the donor emission should substantially overlap with the acceptor absorption spectrum; and (iii) the relative orientation

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of the donor and acceptor transition dipoles should be favorable for coupling. When these conditions are fulfilled, excitation energy can be transferred rapidly and efficiently without photon emission.

Systems that mimic natural light capture, called artificial light-harvesting systems (ALHSs), are connected together via chemical covalent bonds, and they work really well at gathering and moving energy. Their neat molecular structures let us add way more energy donors than acceptors, creating a strong antenna effect and letting the materials absorb more light. Also, the light-absorbing molecules stay very close to one another, so energy can pass between them at a high rate and flow steadily to the reaction center. All these good points make covalent ALHSs perfect models to copy the fast, one-way energy transfer we see in plant photosynthesis.

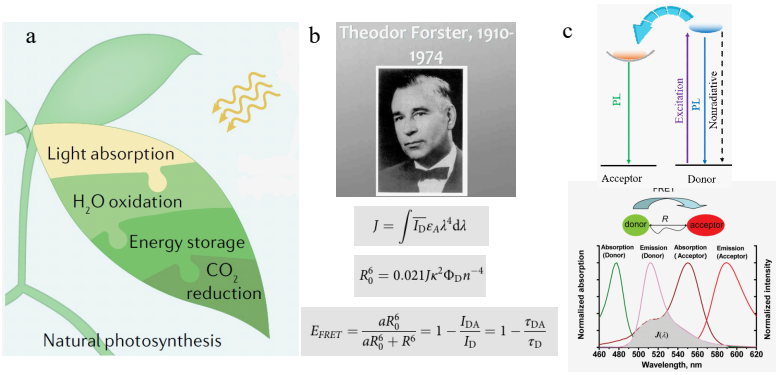

Figure 1. (a) The simple photosynthesis process inside green plants (b) Equations used to compute three different energy transfer pathways (c) How FRET works. R stands for the separation distance between energy donor and acceptor, and *J(λ)* describes how much the donor's emission spectrum overlaps with the acceptor's absorption spectrum [1, 2]

Triplet-to-singlet Förster resonance energy transfer, or TS-FRET for short, is a light-related physical reaction. During this process, energy moves from a donor molecule in its triplet excited state to an acceptor molecule at its ground singlet state, leaving the acceptor in a singlet excited state. Normal singlet-singlet FRET (SS-FRET) follows the reaction $^1D^* + {}^1A \rightarrow {}^1D + {}^1A^*$. Here the excited singlet donor passes energy to the acceptor. TS-FRET works differently with the route $^3D^* + {}^1A \rightarrow {}^1D + {}^1A^*$. It turns long-lasting triplet excitation into singlet fluorescence signals. Thanks to this shift, the slow, delayed light emission from the donor can be turned into long-lived fluorescent light coming from the acceptor.To get high-efficiency TS-FRET, we need to meet four main requirements. First, the donor has to give out obvious phosphorescence, so enough triplet excitons can form. Second, the donor's phosphorescence spectrum needs to overlap a lot with the acceptor's absorption spectrum, which helps energy transfer go smoothly. Third, the space separating donor and acceptor molecules should stay within several nanometers. Fourth, the transition dipoles of both molecules need to face a suitable direction to strengthen dipole-dipole interactions.

Making TS-FRET structures via supramolecular self-assembly is a really promising method, as shown in previous studies [3, 4]. Molecules bind together by weak noncovalent forces in these self-assembled structures. This limits molecular vibration and cuts down energy loss from non-radiative decay, which keeps triplet excitons stable and makes their lifespans longer. Meanwhile, the neat, tight space formed during assembly puts donors and acceptors close to each other, letting energy move quickly. This kind of structure works perfectly for delayed sensitization and TS-FRET effects.

To build supramolecular TS-FRET systems, we first need good room-temperature phosphorescence (RTP) donors. These donors should have high quantum efficiency and long emission time. Only then can triplet-singlet transitions gain enough oscillator strength with strong

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spin-orbit coupling. Most organic phosphorescent donors are designed following El Sayed's rule. We add heteroatoms or aromatic carbonyl groups with lone electron pairs to molecule segments. These groups switch orbital types while changing spin multiplicity. Adding heavy nonmetal atoms like chlorine, bromine or iodine is another popular way to boost spin-orbit coupling and make RTP brighter [5, 6]. Besides that, researchers use many ways to slow molecular movement and reduce non-radiative energy loss when making RTP donors. These methods include crystallization [7], polymerization [8], mixing molecules into hard polymer frameworks [9], and host-guest molecular interactions [10].

As shown in figure 2, acceptors for TS-FRET systems are also required to have small Stokes shifts to minimize spectral energy loss during the triplet-to-singlet energy transfer process [11, 12]. Typically, macrocyclic compounds such as CB[n] (n = 7, 8), β/α-cyclodextrins (β/α-CD), amphiphilic sulfonated calix [4]arenes (SC4A[n], n = 4, 6, 12), as well as functional polymers including PVA, PAA, PMMA, PVP, modified HA, PEG-b-PPG-b-PEG, namely F127 and LP can encapsulate or co-assemble with guest molecules to boost phosphorescence. Efficient energy transfer can be realized after introducing appropriate fluorescent acceptors.

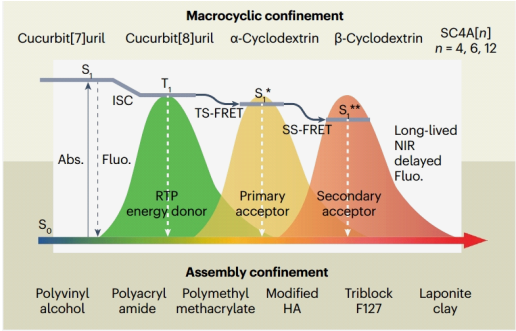

Figure 2. Minimal Jablonski sketch delineating multi-step TS-FRET events regulated by cyclic host confinement and supramolecular packing constraints [13]

2. Solid-state supramolecular TS-FRET systems

To construct solid-state supramolecular TS-FRET systems, it is essential to facilitate intersystem crossing (ISC), restrict molecular motions to reduce non-radiative relaxation for efficient RTP emission, and meanwhile minimize triplet exciton suppression triggered by molecular oxygen [13, 14]. The ongoing optimization involves selecting eligible chromophoric acceptors with matched electronic energy levels and fine-controlling donor–acceptor spacing. For instance, rigid polymeric matrices allow the incorporation of phosphorescent donor and acceptor species through either covalent conjugation or noncovalent intermolecular interactions or phosphorescent functional groups can be grafted onto polymer backbones through copolymerization. These facile strategies suppress non-radiative decay pathways and regulate the spatial arrangement of doped molecules through diverse noncovalent forces, including hydrogen bonding and interfacial interactions between dopant molecules and polymer substrates. Such structural modulation endows the systems with high-performance multicolor afterglow luminescence. Benefiting from these superior characteristics, the developed materials exhibit promising applicability in printing technology, humidity detection, information security encryption and numerous other scenarios. Following this design idea, scientists have created brand-new fully organic TS-FRET materials with longer phosphorescence lifetime and higher quantum yields [15].

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The energy-gap law tells us that when the light wavelength shifts toward longer redder light, the energy of triplet excited states drops. This speeds up non-radiative energy loss and weakens phosphorescence a lot [16-19]. That's why it's still hard to get bright red and near-infrared (NIR) room-temperature phosphorescence (RTP). Artificial light-harvesting systems (ALHSs) offer a useful way to make NIR phosphorescent materials that glow for a long time. As shown in Figure 3a, Yu's research team [20] picked poly(acrylamide-co-vinylcarbazole), short for PAMCz, as the energy donor. This copolymer has really long-lasting RTP. They chose several widely used fluorescent dyes as acceptors, including BODIPY derivatives, Rhodamine B and Cy5, and built an ALHS phosphorescent system. There are three separate chain-like FRET energy transfer routes inside this four-component mixture: PAMCz transfers energy to BODIPY, then Rhodamine B, and finally Cy5 PAMCz transfers energy to alanine-modified BODIPY, then Cy5 PAMCz transfers energy to Rhodamine B, then Cy5

Thanks to these multiple energy transfer paths, the material gives off both white and near-infrared phosphorescence, and its phosphorescence can last as long as 2.7 seconds. Unlike ordinary single-path TS-FRET, this multi-step cascade TS-FRET has many perks. It creates a stronger antenna effect, allows us to adjust emission color across a wider range, and makes the final acceptor glow brighter and longer. Besides, these materials change their luminescence when exposed to outside triggers, so they work really well for hiding and encrypting secret information.

Figure 3b shows another study from Ben Zhong Tang's team [21]. They built a multi-step TS-FRET system inside poly(vinyl alcohol) (PVA) film. The donor was a bromine-containing carbazole molecule that emits long-lived blue RTP. Rhodamine B acted as the middle acceptor, while Cy5 or Cy7 served as the final near-infrared acceptors. By carefully adjusting how much donor and acceptor they mixed, they produced persistent afterglow covering visible light all the way to NIR wavelengths.

Two-step sequential TS-FRET transfers energy more efficiently than the one-step version. It also produces more luminescent colors and raises the quantum yield of the final NIR acceptor greatly. Since these polymer materials dissolve in water, glow for an extremely long time with multiple colors, and keep stable NIR phosphorescence, they are very promising for high-level anti-counterfeiting marks and secure information storage.

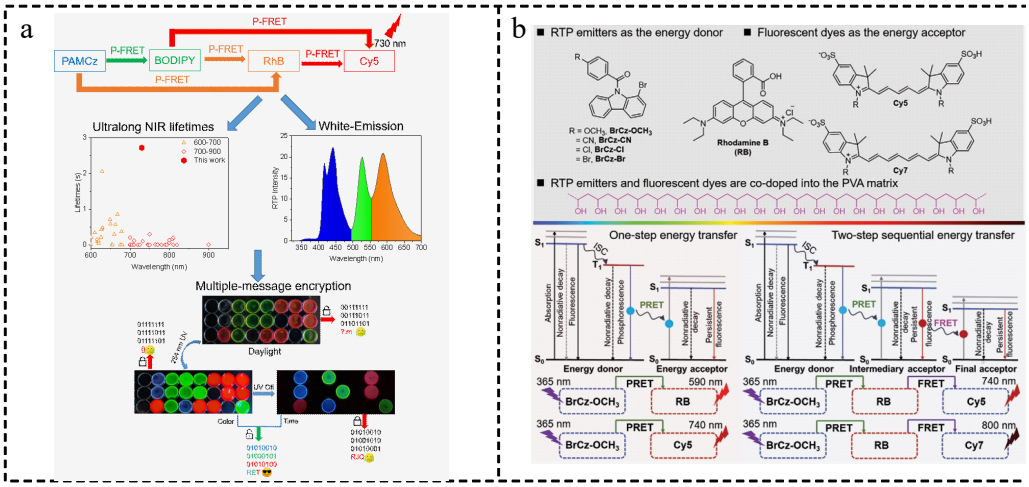

Figure 3. Near-infrared phosphorescence emission system based on FRET. (a) ALHSs coexisting directly and sequentially with FRET [18] (b) Sequential FRET system with phosphorescent emission [19]

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3. Supramolecular TS-FRET systems in aqueous solution

Compared with solid states, triplet excited-state excitons are prone to rapid deactivation in aqueous environments due to the quenching effects of water molecules and dissolved oxygen [22]. Therefore, effective isolation of phosphors from aquatic moisture and oxygen impurities is highly required. Meanwhile, donor and acceptor moieties should maintain ordered spatial arrangement to reduce energy loss [23, 24]. Currently, a prevalent strategy is to co-assemble luminophores with macrocyclic compounds including cucurbit [7, 8] urils, β-/α-cyclodextrins and SC4A [4, 6, 12] to prepare RTP-emissive materials. Large ring host molecules can block non-radiative energy loss of light-emitting guest molecules. They wrap guests away from water and lock molecular structures in fixed shapes, so the samples can produce strong phosphorescence. As shown in Figure 4, Yu Liu's team from Nankai University [25] mixed dibromophthalimide guest molecules (G) and cucurbit [7] uril (CB [7]) in water to make simple two-part aggregates. This original mixture only gave faint room-temperature phosphorescence at 505 nm. Then they added amphiphilic SC4A12 into G⊂CB [7] to form three-component assemblies named G⊂CB [7] @SC4A12. All these tiny assemblies look like evenly sized spheres. After adding SC4A12, the phosphorescent brightness at 505 nm became 40 times stronger, and the emission lifetime stretched to 1.13 ms. Later, researchers added two kinds of fluorescent dyes into the spherical structures to build step-by-step TS-FRET systems that glow near-infrared light. RhB or DBT worked as medium energy acceptors, and Cy5 or NiB were used as final acceptors.The final aggregates can emit light from 425 nm to 800 nm and hold long-lasting phosphorescence. This feature makes them great candidates for cell imaging with different luminescent colors.

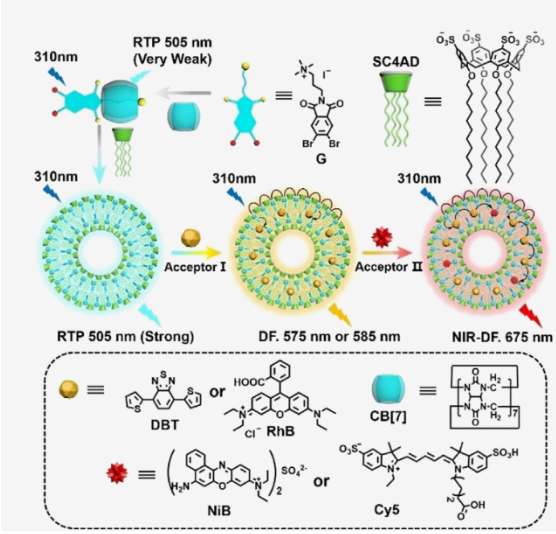

Figure 4. TS-FRET system in aqueous solution [23]

4. Hydrogel-based TS-FRET platforms

Supramolecular hydrogels feature a three-dimensional network structure, which is self-assembled from water-soluble molecular building blocks [26, 27]. Different from aqueous solutions, phosphorescent molecules can directly participate in hydrogel network formation, which restricts molecular motions and effectively isolates quenching species such as dissolved oxygen [28, 29]. This is of great significance for the further development and application of long-lived multicolor luminescent soft materials. As shown in figure 5, the Liu Yu group [30] obtained weak

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phosphorescence emission (lifetime: 442 μs) at 510 nm via the co-assembly of dimethylvinylbromopyridinium derivatives (G) with CB [8]. The G/CB [8] assemblies served as supramolecular crosslinkers for the in-situ copolymerization with acrylamide, followed by co-assembly with hydroxypropyl-β-cyclodextrin-modified hyaluronic acid (HA-HP-β-CD) to form double-network hydrogels. The hydrogel matrix provided an optimized confined microenvironment for phosphorescence, This strategy elongates the phosphorescence duration from 442 μs to 5.17 ms while drastically boosting the phosphorescent emission intensity. Furthermore, ALHSs based on single-step TS-FRET were fabricated by doping ESY as acceptors into the hydrogel. The lifetime of delayed fluorescence of ESY at 560 nm was significantly prolonged to 36.4 μs. Benefiting from the long-lived photosensitizers and confined microenvironment, the as-prepared ALHSs exhibited 1.9-fold higher photocatalytic activity than pure ESY.

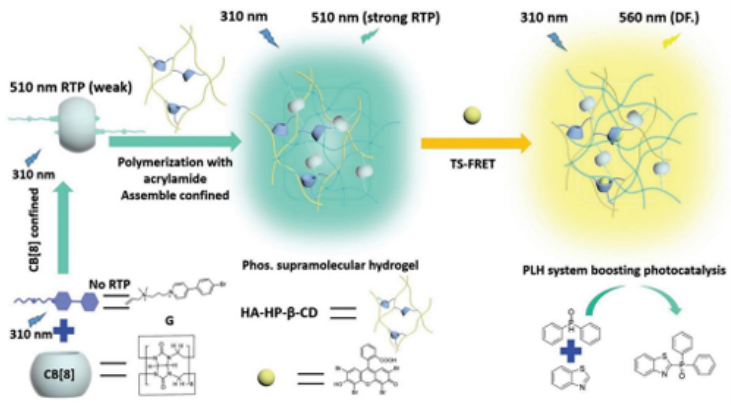

Figure 5. TS-FRET system in hydrogel [30]

5. Conclusion and outlook

Organic room-temperature phosphorescent materials can be used in many different areas. For most ordinary organic molecules, spin-related rules stop singlet excited states (S_1) from turning into triplet states (T_1) directly through intersystem crossing. Besides, those long-lived triplet states easily lose energy without releasing light, and dissolved oxygen can also destroy the excited excitons. That's why normal organic compounds barely show phosphorescence unless we cool them down to very low temperatures like 77 K or store them inside argon gas with no air.Lots of researchers have tried hard to fix these problems in recent years. Carefully controlling how molecules gather together helps us make phosphorescent materials that work at room temperature based on crystal structures. People have come up with several ways to lock molecular structures tightly, including crystal design, wrapping molecules in polymers and supramolecular assembly. These methods reduce energy loss of triplet excitons and help materials produce bright phosphorescence. Förster resonance energy transfer, or FRET, works well to make up the weak points of regular RTP materials. Plenty of previous papers prove this energy transfer process can stabilize the triplet state of acceptor molecules. It makes phosphorescence brighter and lets the light last longer at the same time.

In the future, we need to find better ways to control triplet excitons and build multiple energy transfer channels that work together. We also need to design better confined microenvironments to raise phosphorescence efficiency, extend emission lifetime and make materials more stable when being used. At the same time, we can combine stepwise TS-FRET systems with new optical properties. Examples include chiral glowing, circularly polarized luminescence, color change

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triggered by outside conditions and multi-dimensional data encryption. This will greatly widen the uses of long-afterglow materials. With these improvements, we might create smart luminescent materials that glow for a long time, emit near-infrared light and show various optical signals.

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