Organic Fluorophores Exhibiting Highly Efficient Photoluminescence in the Solid State

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[Image: Diagram showing various applications of organic fluorophores, including light-emitting diodes, solid-state lasers, light-emitting field-effect transistors, and solid-state luminescent sensors.]
Abstract: There has been extensive research on the development of organic optoelectronic devices, such as organic light-emitting diodes, organic field-effect transistors, and organic solid-state lasers from various viewpoints, ranging from basic studies to practical applications. As organic materials are used as solids in these devices, the importance of organic chromophores that exhibit intense emissions of visible light in the solid state is greatly increasing in the field of organic electronics. However, highly efficient emission from organic solids is very difficult to attain because most organic emitting materials strongly tend to cause concentration quenching of the luminescence in the condensed phase. Therefore, in order to generate and improve organic optoelectronic devices, it is necessary to design novel chromophores that exhibit superior solid-state emission performance. This Focus Review covers the recent development of highly emissive organic small molecules whose photoluminescence quantum yields in the solid state have been reported. Following the introduction, the photophysical processes of excited molecules are briefly reviewed. Subsequently, organic solid fluorophores are described with an emphasis on the characteristics of their molecular structures.

Keywords: chromophores · fluorescence · materials science · molecular electronics · photophysics

1. Introduction

Efficient solid-state emission of organic materials is essential for optoelectronic devices, such as organic light-emitting diodes (OLEDs),[1] organic light-emitting field-effect transistors (OLEFETs),[2] organic solid-state lasers,[3] and organic fluorescent sensors (Figure 1).[4,5] Hence, the molecular design and development of novel chromophores that emit visible light in the solid state with high efficiency are strongly desired for the realization, modification, and advanced applications of such optoelectronic devices with superior performance.[6]

Measurement of the photoluminescence (PL) quantum yield of an organic chromophore in solution is well-established and easy to perform, whereas measurement of the absolute quantum yield of an organic emitter in the solid state with high accuracy is quite complicated[7] because of the difficulties in determining the angular dependence of the emission, reflectivity, and absorption caused by anisotropy and the waveguiding effect of organic solids.[8] Therefore, one primary parameter for choosing organic emitters employed in such optoelectronic devices has conventionally been the PL quantum yield in solution. However, most organic chromophores are non-luminescent or only faintly emissive in the solid state, even if they are highly emissive in solution, owing to the concentration quenching caused by intermolecular interactions such as excimer formation and energy transfer in the condensed phase. As a result, most emitting organic materials that are employed in optoelectronic devices are used as dopants at low concentration (a few percent) in the host material. Furthermore, a totally opposite event has recently been reported in which a π-conjugated molecule that is non-emissive in solution becomes highly emissive in aggregated states, such as thin films, nanoparticle suspensions in poor solvent systems, powders, and crystals.[9] This unique phenomenon has been coined as aggregation-induced emission by Tang and co-workers.[10] Therefore, it is truly inappropriate to refer to the PL quantum yield in solution as one of the guidelines for selecting organic emitting solids for device applications. It is apparent that the solid-state quantum yield is an essential and reliable parameter for estimating and analyzing the total luminescence efficiency of organic optoelectronic devices. In addition, the solid-state quantum yield is indispensable for understanding fundamental solid-state photophysics, such as in radiative and non-radiative processes. The great significance of, and demand for, solid-state quantum efficiency has led to the development of several methods that utilize an integrating sphere for fast and accurate measurement of the absolute quantum yield.

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The use of an integrating sphere is beneficial for overcoming the difficulties that originate from the characteristics of organic solids and for eliminating the need to use a standard chromophore as a reference. Hence, owing to advances in analytical methods, studies on the development of highly emissive organic solids that can be applied to non-doped type optoelectronic devices are greatly accelerated using the solid-state quantum yield as a principal parameter for estimating the validity of the novel molecular design and the potential of the designed molecules as superior emitters.

This Focus Review highlights recent studies on highly fluorescent small organic molecules in which the PL quantum yields of the chromophores in non-doped solid states, such as crystal, neat film, and powder have been reported. The notations $\Phi_{\text{crystal}}$, $\Phi_{\text{film}}$, and $\Phi_{\text{powder}}$ express the quantum yields of the crystal, neat film, and powder of the fluorophores, respectively. The small fluorophores are classified by their emission color and described with emphasis on the characteristics of their molecular structures. Luminescent polymers, as well as phosphorescent dyes for which several reviews are available, are not covered in this review.

2. Photophysical Processes of Excited Molecules

Fluorescence is only one of the many possible electronic processes that excited molecules can undergo. Hence, it is essential to suppress other non-radiative processes, such as internal conversion (IC), intersystem crossing (ISC), electron transfer, energy transfer, and excimer/exciplex formation in order to attain highly efficient fluorescence. This section provides a brief overview of the characteristics of these electronic processes.

2.1. Fluorescence and Non-Radiative Processes in a Molecule

The Jablonski diagram is very useful for illustrating the photophysical processes of an excited molecule, including its generation (Figure 2). A molecule in the ground state ($S_0$) is excited to one of the vibrational levels of the excited state ($S_1$) by absorbing a photon of light or by the recombination of an electron ($e^-$) and a hole ($h^+$). The excited molecule reaches the lowest vibrational level of $S_1$ with a time scale of $10^{-13}$–$10^{-11}$ seconds by vibrational relaxation (VR) owing to conformational change and/or collisions with surrounding molecules. The decay process that accompanies the emission of a photon from the lowest $S_1$ state to one of the vibrational levels of $S_0$ is termed fluorescence (FL). Owing to energy consumption through VR from the initially excited state to the lowest $S_1$ state, the fluorescence spectrum appears at longer wavelengths than those of the absorption spectrum. In addition to radiative decay, several non-radiative decay pathways are also possible from the lowest $S_1$ state, which result in a decrease in the fluorescence, or so-called fluorescence quenching. One is internal conversion (IC) to a higher state...
vibrational level of the $S_0$ state followed by VR. The other pathways start by intersystem crossing (ISC) to a higher vibrational level of the $T_1$ state. Although electronic transition between states of different multiplicities is theoretically not allowed, intersystem coupling such as $S_1 \rightarrow T_1$ is possible because of spin-orbit interactions. The presence of a heavy atom is known to facilitate spin-orbit interactions and hence intersystem crossing. VR of the molecule from a higher $T_1$ state to the lowest one may be followed by forms of radiative decay, such as phosphorescence (Phos), triplet-triplet annihilation in which the triplet molecule returns to the $S_1$ state, and/or intersystem crossing to a higher level of $S_0$ with subsequent VR. Although revival of the $S_0$ state in a molecule by T–T annihilation may afford an opportunity for the radiative decay process known as delayed fluorescence, the energy loss of another molecule is apparently inevitable for the re-excitation process.

In the solid state, molecules can form aggregates whose structure affects fluorescence properties such as emission wavelength and efficiency. Hence, it is also important to consider the two possible transitions of a physical dimer that consists of two identical molecules positioned close to one another in a specific three-dimensional arrangement without a chemical bond: the J-aggregate and the H-aggregate (Figure 3). When two molecules are aligned in a head-to-tail manner, the aggregate is called a J-aggregate. On the other hand, the H-aggregate involves a parallel arrangement of the two molecules. The formation of a physical dimer results in the splitting of the excitation level into two levels: one lower and another higher than that of the monomer. When the transition dipoles of the monomers (illustrated by the arrows in the dotted rectangles in Figure 3) cancel out because of their opposing directions, the transition to and from one level is forbidden. In contrast, the transitions to and from the other level is optically allowed if coupling of the dipoles results in a nonzero transition moment. For the J-aggregate, the lower level of the exciton is allowed so that fluorescence is favored and red-shifted compared with that of the monomer. On the other hand, the allowed transition in the H-aggregate is to the upper level. Hence, the H-aggregate shows a blue shift in fluorescence relative to the monomer. It also exhibits low luminescence efficiency because the exciton energy can be consumed by VR from the upper to the lower level, from which the radiative transition is forbidden. In short, the J-aggregate is advantageous for efficient solid-state fluorescence, whereas the H-aggregate is detrimental to it.

2.2. Intermolecular Non-Radiative Processes of Excited Molecules

Intermolecular interactions of excited molecules in the solid states with the surrounding molecules, including electron transfer, energy transfer, and excimer/exciplex formation can also cause fluorescence quenching of the initially excited chromophores. Electron transfer is classified into two patterns, as illustrated in Figure 4. One is an oxidative process in which an electron is transferred from an excited molecule ($D^*$) to an acceptor molecule ($A$), resulting in the generation of the oxidized donor ($D^\cdot$) and the reduced acceptor ($A^\cdot$). The other pattern involves reductive electron transfer, in which an excited molecule accepts an electron from a donor molecule, thus producing the same species as in the oxidative process.

Dimers formed from an excited molecule ($M^*$) and the identical molecule in the ground state ($M$) are called excimers (the term coming from ‘excited dimer’ [Eqs. (1) and (2)]). Fluorescence emission from an excimer is observed as

$$M^* + M \rightarrow (MM)^* \text{ excimer} \quad (1)$$

$$M^* + N \rightarrow (MN)^* \text{ exciplex} \quad (2)$$

a broad and structureless band at a wavelength longer than that of the monomer fluorescence. Thus, the emergence of excimers causes quenching of the intrinsic fluorescence of $M^*$. Excimer formation depends on the concentration of the chromophore and is thus a particularly critical issue to consider for fluorescence quenching in the solid state. Exciplexes (the term coming from ‘excited complex’) are complexes between an excited molecule ($M^*$) and a ground-state mole-
cule of a different compound (N) and also show broad fluorescence spectra in the lower energy region. In optoelectronic devices, exciplex formation can occur at the interface of the emitting material layer and the adjacent organic layers.\cite{16}

The transfer of excitation energy from an excited molecule to an acceptor molecule can occur via Coulombic and/or intermolecular orbital overlap interactions (Figure 5).

\[
D^* + A \rightarrow D + A^* \quad (3)
\]

The energy transfer mechanism based on Coulombic interactions is called the Förster mechanism and the essence of the transfer is a dipole-dipole interaction. Thus, de-excitation of an electron located in the LUMO of the donor* to the HOMO, and excitation of an electron located in the HOMO of an acceptor occur simultaneously, giving rise to a pair consisting of a ground-state donor and an excited acceptor. The energy transfer occurs efficiently when the overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor, as well as the molar absorption coefficient of the acceptor, are both large. The energy transfer can be effective at long distances up to circa 100 Å; the transfer rate constant is proportional to the inverse sixth power of the distance. On the other hand, when the intermolecular orbital overlap of a donor and an acceptor is large enough to affect electronic communication, an energy transfer through electron exchange, called the Dexter mechanism, becomes possible. The excited electron in the donor* and one of the two electrons in the HOMO of an acceptor are exchanged as illustrated in Figure 5. Owing to the physical contact of the donor and acceptor molecules, the energy transfer via the Dexter mechanism is operative at a short range (ca. 10 Å); the rate constant is an exponential function of the reciprocal of the distance.

When the donor and acceptor molecules are identical, the energy transfer produces the same set of molecules as before the transfer, irrespective of the mechanism (Figure 6). Thus, the population of excited donors (D*) does not change through the energy transfer, and the overall process is called energy migration. Hence, if the photophysical processes of D* are limited only to fluorescence and energy migration, the fluorescence efficiency should be unity (Figure 6a). On the other hand, if non-radiative pathways for D* are operative in addition to fluorescence and energy migration, then energy migration clearly amplifies the opportunities for energy loss, and thus results in a decrease in fluorescence efficiency.

### 2.3. Fluorescence Quantum Yield

The efficiency of fluorescence emission is evaluated by the fluorescence quantum yield (\(\Phi\)), defined as the ratio of the number of photon-emitted molecules to the number of excited molecules.\cite{17} Hence, the maximum value of \(\Phi\) is 1.0. Using the rate constants of photophysical processes (\(k_r\): rate constant for radiative decay, \(k_{nr}\): rate constant for non-radiative decays), \(\Phi\) can be defined by the equation: \(\Phi = k_r / (k_r + k_{nr})\).

Consequently, in order to develop new organic fluorophores that exhibit excellent luminescence efficiency in the solid state, it is crucial that the molecular design allows for the reduction of potential non-radiative decay processes in condensed phases. In the next section, recent progress on the development of organic small molecules that exhibit highly efficient fluorescence in the solid state will be reviewed.
3. Highly Fluorescent Organic Solids

3.1. Blue- and Green-Light-Emitting Organic Fluorophores

The incorporation of a spiro framework into a small molecule is advantageous for improving solubility and morphological stability as well as suppressing close-packing in the solid state.\[18\] Oligophenyls exhibit a large Stokes shift that implies a small overlap between the absorption and emission spectra, and thus induce suppression of Förster-type energy transfer. Application of the spiro concept to oligophenyl moieties led to the design of spiro-sexiphenyl 1 as a dye for solid-state lasers. Amorphous and polycrystalline films of 1 emit blue light with $\Phi_{\text{film}}$ of 0.40 and 0.60, respectively (Scheme 1).\[19\] The amorphous film is thermally stable owing to the high glass transition temperature ($T_g$) of 212°C. The planarity of the fluorene moieties that contain the spiro linkage imparts rigidity and extended $\pi$-conjugation between the central two benzene rings of each sexiphenyl chromophore. This decreases the potential pathways for non-radiative decay. At the same time, the freedom of intramolecular rotation of the terphenyl moieties at the molecular terminus is indispensable for keeping the Stokes shift large enough to suppress energy transfer from the excited state by the Förster mechanism. Because 2,2,7,7-tetrabromo-spirobifluorene is commercially available (and can be readily prepared by bromination of spirobifluorene), various symmetrical and unsymmetrical spirobioligophenyls have been synthesized and characterized as organic emitters. However, in nearly every case, the photoluminescence quantum yields in the solid state have not been reported.\[18\]

Highly efficient blue emission has been demonstrated with ter(9,9-diarylfluorene)s 2 in vacuum-deposited thin films, which are thermally and electrochemically stable owing to the installation of two benzene rings at the 9-position (Scheme 2).\[20\] The temperature producing a 5% weight loss upon heating ($T_d$) ranges from 400 to 450°C, and the electrochemical redox reactions are reversible. An orientation of the aryl groups at the 9-position, perpendicular to the fluorene plane, renders the $\pi$-conjugated planes distant from the adjacent chromophores, and effectively prevents intermolecular orbital interactions. Electroluminescence (EL) devices using 2a and 2b as a blue-emitting layer respectively recorded high EL external quantum efficiencies of 4.1 % and 5.3 %, high brightness of approximately 8000 and 14000 cd/m², and low turn-on voltages of approximately 2.5 V.\[21\] The high EL efficiencies are consistent with the high PL quantum yields, indicating that the PL quantum yield in the solid state is as a reliable parameter for estimating the potential of the designed solid fluorophores.

A molecular design involving disubstitution of aromatic rings at the 9-position of fluorene is also effective for developing ultraviolet (UV) emitters that exhibit high solid-state quantum yields, high morphological and thermal stabilities, and reversibility of electrochemical redox processes (Scheme 3).\[22\] Thus, thin films of bi(9,9-diarylfluorene)s 3a and 3b produced strong PL emissions of UV light (emission maxima: 392 and 393 nm, respectively) with high $\Phi_{\text{film}}$ values of 0.66 and 0.60, respectively. Therefore, the potential of 3 and related bifluorene derivatives as UV emitters for OLEDs and host materials for red electrophosphorescence devices has been verified. A similar level of UV-photoluminescence efficiency in the solid state has been observed with 9,9-dimethyl-2,7-diphenyl-9-silafluorene ($\lambda_{\text{max}} = 379$ nm, $\Phi_{\text{film}} = 0.65$).\[23\]

Diphenylamino- and 4-(N-phenylbenzimidazol-2-yl)phenyl-substituted fluorene 4 serves as a blue emitter ($\lambda_{\text{max}} =$...
466 nm) with high efficiency ($\Phi_{film} = 0.80$) and thermal stability ($T_{d} = 373{ }^\circ$C; Scheme 4). In addition, 4 exhibits electron and hole mobilities of approximately $10^{-3} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ owing to the presence of the triarylamine and ($N$-phenyl-benzimidazol-2-yl)benzene moieties, respectively. These characteristics allowed the fabrication of OLED devices using 4 as the sole organic component without organic hole- and electron-transporting layers; a single-layer device recorded an external EL quantum efficiency of 2.4%, a luminance of 2378 cd/m$^2$, and a turn-on voltage of 2.9 V at 100 mA cm$^{-2}$. Spirobifluorene substituted by the same donor and acceptor at the 2- and 7-positions, respectively, has been applied to OLEFETs for white emission.[25] When two 9,9-diarylfluorene moieties are connected with 2,1,3-benzothiadiazole as a spacer, the resulting chromophore (5) in thin film shows green fluorescence ($\lambda_{\text{max}} = 544$ nm) with a high $\Phi_{film}$ of 0.81 (Scheme 5).[26] The design of the donor-acceptor-donor structure using 2,1,3-benzothiadiazole as the acceptor enables the green emission, and the high $\Phi_{film}$ is again explained by the steric effects of the diarylfluorene moieties. EL devices using 5 as a non-doped green emitter have been characterized, and the highest external quantum efficiency is reportedly 3.7% at 100 cd/m$^2$. 2,5-Diphenylated thiophene-$S,S$-dioxide 8 and 2,5-dibiphenylated thiophene-$S,S$-dioxide 9 also show intense solid-state emission at shorter wavelengths than those of 6 and 7, respectively. Neat thin films of 2,3,4,5-tetraarylsiloles 10-13 exhibit intense fluorescence with excellent quantum yields in the region of blue to green light (Scheme 7). The tetrasubstitution of aromatic rings at the ring carbons of siloles induces distorted conformations of the incorporated rings in relation to the silole plane owing to steric repulsion between the adjacent rings. As a result, the nonplanar molecular structures suppress intermolecular interactions, leading to concentr-
tion quenching in the solid state. Since siloles have low-lying LUMOs, owing to $\sigma^* - \pi^*$ conjugation between the $\sigma^*$ orbitals of the two exocyclic silicon–carbon bonds and the $\pi^*$ orbital developed over the butadiene moiety,[30] emissive siloles can act as electron-transporting emitters in OLED devices. When the bilayer film of 10 and $N,N'$-di(naphthalene-2-yl)-$N,N'$-diphenyl(1,1'-biphenyl)-4,4'-diamine was prepared, the PL emission maximum of the film, observed at 495 nm, was red-shifted by approximately 20 and 50 nm, respectively, relative to those of electron-acceptor 10 and the electron-donating diamine.[31] Hence, the red-shifted luminescence can be assigned to an emission from exciplex formation between 10 and the diamine. The quantum efficiency of the bilayer film ($\Phi_{\text{film}} = 0.62$) is remarkable because exciplex emission is generally inefficient.

The relationship between solid-state emission and the molecular structures of 2,5-bis(silylethynyl)-3,4-diphenylsiloles has also been systematically investigated.[32] When the alkyl groups on the ethynylated silicon atoms become larger, the emission color is blue-shifted and the quantum yield of the solid-state emission generally increases. The highest $\Phi_{\text{powder}}$ (0.999) was recorded by an amorphous powder of 2,5-bis(triisopropylsilylethynyl)-3,4-diphenylsilole (14, Scheme 8).

The bulky triisopropylsilyl groups inhibit close packing and induce an antiparallel arrangement of the adjacent molecules, which effectively suppresses intermolecular electronic interactions and intramolecular rotations. This packing behavior sharply contrasts with the observation that incorporation of triisopropylsilylethynyl groups into pentacene induces the dense stacking of the resulting pentacene derivative.[33]

The spiro concept is also applicable to 9-silafluorenes (Scheme 9).[34] As a neat film, spirobisilafluorene 15 exhibits blue fluorescence ($\lambda_{\text{max}} = 410$ nm, $\Phi_{\text{film}} = 0.54$) with a $T_1$ of 228°C.[35] Although its synthesis requires several steps, the asymmetric installation of tert-butyl and biphenyl groups into the spiro-linked fluorene skeletons is the key to its superior morphological stability. It would be intriguing to install a donor and an acceptor instead of tert-butyl and biphenyl groups to realize solid-state fluorescence with an emission maximum at longer wavelengths than those of the blue region.

Arene-fused siloles, such as 3,2'-silicon bridged 2-phenylindole[36] $N$-phenylbenzof[$\pi$]silole[37] and carbon- and silicon-bridged ladder stilbene[38] are also blue-emissive fluorophores (Scheme 10). In the case of 16, aggregation-induced emission is observed and excellent quantum yields are recorded in various solid states. The bulky isopropyl groups, oriented perpendicular to the completely flat tetracyclic chromophore, render the adjacent molecules far from one another with an almost orthogonal arrangement in the crystals. Because 3,2'-silicon-bridged 2-phenylindoles can be synthesized in high to excellent yields by palladium-catalyzed intramolecular coupling of the corresponding 2-(2-indolylsilyl)aryl triflates, a variety of functionalized derivatives that exhibit intense blue fluorescence are readily available.[39] When the diphenylsilene group in 17 was replaced by dimethylsilylene, the $\Phi_{\text{powder}}$ dropped from 0.78 to 0.46. Hence, the phenyl groups on the silicon, each tilted by 38.2° from the silole plane, are essential for attaining a high $\Phi_{\text{powder}}$ value. The high $\Phi_{\text{crystal}}$ of 18, relative to that of its diphenylmethylene- and dimethylsilylene-bridged counterparts ($\Phi_{\text{crystal}} = 0.22$) is attributed to the propyl substitution at both the carbon and silicon bridges, which induces parallel packing of 18 with a $\pi$-plane distance of 7.3 Å in the crystal.

$N$-Methyl-2,3-diarylindoles in the powder are known to exhibit blue fluorescence, with quantum yields ranging from 0.44 to 0.97.[40] In particular, bis(trifluoromethyl)-substituted indole 18a, for which the benzene rings at the 2- and 3-positions are distorted from the indole plane by 45° and 43°, respectively, records excellent $\Phi_{\text{powder}}$, as shown in Scheme 11. As the examples are limited, the importance of the presence of a trifluoromethyl group is unclear and required further study.

Single crystals of 1,4-distyrylbenzene with herringbone packing, prepared by the physical vapor transport (PVT) method, emit blue light (468 nm) with good $\Phi_{\text{crystal}}$ (0.65).[41] When two phenyl groups are introduced at the 2,5-positions

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\lambda_{\text{max}} = 410 \text{ nm} \\
\Phi_{\text{film}} = 0.54
\]

\[
\lambda_{\text{max}} = 434 \text{ nm} \\
\lambda_{\text{max}} = 433 \text{ nm} \\
\phi_{\text{crystal}} = 0.91 \\
\lambda_{\text{max}} = 414 \text{ nm} \\
\Phi_{\text{film}} = 0.90
\]

\[
\lambda_{\text{max}} = 410 \text{ nm} \\
\Phi_{\text{powder}} = 0.78
\]

\[
\lambda_{\text{max}} = 475 \text{ nm} \\
\phi_{\text{crystal}} = 0.63
\]

Scheme 10. Blue-emissive fused siloles.
of the central benzene ring in 1,4-distyrylbenzene, recrystal-
lization of the resulting benzene 19a from a CHCl₃/MeOH solution affords needle-like crystals that exhibit an enhanced ϕ<sub>crystal</sub> of 0.80 and an emission maximum at 444 nm (Scheme 12).<sup>[42]</sup> The excellent ϕ<sub>crystal</sub> is explained by cross-di- ploe stacking wherein the angle between the long axes of
two overlapped molecules is 70°. In contrast, the emission efficiency of slice crystals of 19a obtained by the PVT method dropped to 0.48, presumably owing to J-stacking. Al-
though the ϕ<sub>crystal</sub> of the slice crystal is moderate and lower than that of the needle-like crystals, the threshold for amplified spontaneous emission is conversely smaller for the slice crystal than for the needle-like crystal. This observation indicates that the slice crystal may be a better candidate for laser application. Meanwhile, 1,4-bis[(E)-(2-methylphenyl)ethenyl]benzene 19b and 1,4-bis[(E)-(4-methylphenylethenyl]benzene 19c also show intense blue emission in crystals obtained by the PVT method with ϕ<sub>crystal</sub> values of 0.88 and 0.89, respectively.<sup>[43]</sup> The dihedral angle of the ortho-tolyl group and the central benzene ring for 19b in crystal is circa 30°, whilst the entire molecular frame of 19c is almost planar in the single crystal, a feature which results in her-
ringbone-like packing. Amplified spontaneous emission of the crystals is observed with low thresholds; these chromo-
phores are also expected to be superior dyes for laser appli-
cation. As the bis(styryl)benzene framework is easy to pre-
pare, systematic studies of the effect of substituents on both the central and terminal benzene rings on the molecular and
crystal structures in the solid state as well as the emission colors and efficiency would be intriguing.

The introduction of two aryl groups into the central part of a chromophore is also effective for enhancing the PL effi-
ciency of 1,6-diaryl-1,3,5-hexatrienes in the solid state (Scheme 13).<sup>[44]</sup> For example, 3,4-bis(piperidinophenyl)-1,6-bis(4-trifluoromethyl-phenyl)-1E,3E,5E-hexatriene (20) exhibits green fluorescence in powder form with good quantum yield. Because 1,3,4,6-tetraaryl-1,3,5-hexatrienes, includ-
ing 20, are non-fluorescent in solution, the trienes constitute a class of chromophores that exhibit aggregation-induced emission.

Tetraphenylethene derivatives also constitute a class of chromophores that exhibit remarkable aggregation-induced emission.<sup>[45]</sup> In solution, the four phenyl groups can freely undergo intramolecular rotation, causing loss of excitation energy, and thus fluorescence quenching. In contrast, intra-
molecular rotation is severely restricted in the aggregated state, which suppresses non-radiative decay processes. For example, 4,4'-bis(triphenylethenyl)biphenyl (21) is not fluo-
rescent at all in tetrahydrofuran, but is intensely blue- and green-emissive in crystalline fibers and amorphous film, re-
spectively, with excellent quantum yields (Scheme 14). Very recently, the incorporation of tetraphenylethene moieties into pyrene that suffers from aggregation-induced fluores-
cence quenching is demonstrated to render the resulting molecule 22 luminescent in the solid state with a high quanti-
yum yield.<sup>[46]</sup> Hence, combining a chromophore that under-
goes concentration quenching in the solid state and a chro-
mophore that exhibits aggregation-induced emission can serve as a versatile strategy for the development of highly emissive solid fluorophores.

In addition to phenylenevinylene-type emitters, highly emissive oligo(phenyleneethynylene)s in the solid state have also been developed. For example, thin films of 2,5-bis(di-
mesityl)biphenyl)-1,4-bis(4-diphenylaminophenyl)ethenyl]benzene (23) show intense emission at 562 nm with a ϕ<sub>film</sub> of 0.90 (Scheme 15).<sup>[47]</sup> The diborylbenzene 23 is stable against air, water, and heat (T<sub>d</sub> = 373°C). Density functional theory (DFT) calculations suggest that the excited state is gener-
ated by intramolecular charge transfer transition from the HOMO on the long axis of the molecule to the LUMO lo-
calized on the boron—benzene—boron skeleton. Dual incor-
poration of a bulky dimesitylboryl group as an electron-ac-
ceptor<sup>[48]</sup> at the central benzene ring of a bis(phenylethynyl)-
benzene is key to attaining the large Stokes shift (115 nm) and steric protection of the chromophore from electronic interactions with neighboring molecules in the condensed phase, leading to high fluorescence efficiency.

The substitution of two alkoxy groups at the 2- and 5-positions of 1,4-bis(phenylethynyl)benzene 24 also induces solid-state fluorescence with high quantum yields. For example, the hexyloxy derivative 24a shows turquoise emission with a $\Phi_{\text{film}}$ of 0.78 (Scheme 16). X-ray analysis reveal that two molecules of 24 form a J-aggregate in the crystal. Although there is no correlation between the spacing of the two molecules that form the aggregate and the chain length of the alkoxy groups, the emission maximum is linearly red-shifted as the spacing becomes narrower. Methoxy- and cyano-substituted oligo(phenyleneethynylene) 25 in powder also exhibits turquoise emission (Scheme 16). Owing to the difficulty of obtaining single crystals, there is not yet any information on the three-dimensional structure of 25 in the solid state.

As oligofluorenes are blue wavelength emitters and morphological stability as well as high luminescence efficiency, starburst molecules bearing six arms of oligofluorene moieties were designed as blue fluorescent materials (Scheme 17). Triarylamine-cored 26 and truxene-cored 27 show excellent solid-state $\Phi_{\text{film}}$ with longer arms (e.g., trimers and tetramers of 9,9-diarylfluorenes). The ELs of both 26a and 27 are very stable deep-blue emissions. Thus, the potential of 26a as an organic laser material and the utility of 27a as a host material for red electrophosphorescence have been demonstrated.

Dimethyl(pentafluorophenyl)silyl-substituted 9,10-diphenylanthracene 28 shows blue fluorescence at a maximum of 445 nm with excellent $\Phi_{\text{crystal}}$ (0.93) and $\Phi_{\text{film}}$ (0.81) and a small Stokes shift of 9 nm (Scheme 18). X-ray analysis of the single crystal reveals that the fluorinated phenyl groups are stacked with the anthracene skeleton, presumably owing to the arene-perfluoroarene interaction. In addition, the rate constant for non-radiative decay was found to be much smaller than that of the non-fluorinated counterpart. Accordingly, the pentafluorophenyl groups were considered to contribute to the increased rigidity of the molecule in the excited state. It is noteworthy that 28 showed intense solid-state emission given that solid 9,10-diphenylanthracene causes severe fluorescence quenching. On the other hand, the low yield of 28, which is likely due to steric hindrance, remains to be improved for further extension of this concept. Introduction of a diphenylphosphine oxide group into the phenyl groups of 2-tert-butyl-9,10-diphenylanthracene provided the electron-transporting blue-emitting fluorophore 29. The non-planar conformation induces weak intermolecular interactions in the solid state and high morphological stability. Owing to the good electron-affinity of 29, EL devices using 29 do not require an electron-transporting layer. Thus, the double-layer EL device consisting of 29 and 9,9-bis[4-(N,N-diphenylamino)phenyl]fluorene as a hole-transporting layer works well with an EL efficiency of 4.3% (2.9 cdA$^{-1}$) at 1.3 mAcm$^{-2}$.

N,N’-Di(naphthalene-1-yl)-N,N’-diphenyl-[1,1’:4’,1”-quaterphenyl]-4,4”-diamine (30) in neat film has been reported to emit blue light much brighter than that emitted by N,N’-di(naphthalene-1-yl)-N,N’-diphenylbenzidine (tr-NPD), and to harvest triplet excitons to lower-energy emitters for white emission (Scheme 19). Pyrene-substituted triphenylamine 31, which emits intense blue light, has been reported to be a good emitter for application in exciplex-based organo-
For both materials, there is no information about their structural characteristics in the solid state and the photophysical properties of their related derivatives. Preparing the derivatives by transition-metal-catalyzed cross-coupling reactions and N-arylations using aryl halides appears to be straightforward. Therefore, further studies are awaited to disclose the essence of the molecular designs buried in 30 and 31.

A thin film of tetraphenylimidazole 32 and crystals of anthranilic acid 33 shows blue emission (Scheme 20). In the case of 32, substitution of the four aryl groups at an imidazole ring retards the dense packing of the resulting chromophores, and the excited-state intramolecular proton-transfer induces a large Stokes shift (96 nm) which helps to diminish the likelihood of intermolecular energy transfer, leading to a low solid-state quantum yield. The simplicity of tetraphenylimidazole preparation, which involves an acid-catalyzed one-pot reaction of a salicylaldehyde, an aniline, a benzil, and an ammonium acetate, is quite attractive for further molecular modifications. Benzoic acid 33 provides a blue-emissive single crystal in which the acids form dimers, stacked in the manner of J-aggregates, through intermolecu-
lar O–H···O=C hydrogen-bonding and intramolecular N–H···O=C hydrogen-bonding. These structural motifs are advantageous for enhancing molecular rigidity, restricting intramolecular rotation, and thus improving luminescence efficiency in the solid state.

### 3.2. Red-Light-Emitting Organic Fluorophores

Because red emission requires a narrow HOMO–LUMO gap, red fluorophores usually consist of π-extended polycyclic aromatic hydrocarbons, or π-conjugated molecules that are substituted by electron-donating and -accepting groups at the termini of the π-conjugated system. However, red fluorophores in the solid state generally have a strong tendency to cause aggregations that result in fluorescence quenching, owing to the π–π stacking originating from the high planarity or the dipole-dipole interaction induced by the presence of donor and acceptor substituents. For example, 4-(dicyanomethylene)-2-methyl-6-[4-(dimethylamino)styryl]-4H-pyran, which is well-utilized as a red dopant in organic light-emitting devices, reportedly exhibits emission at 665 nm with a quantum yield of 0.05 in neat film. Therefore, it is a challenge to develop red fluorophores with high efficiency in the pure solid state, and realization of quantum yields exceeding 0.3 are notable for non-doped red emitters.

Diphenylamino and dicyanoethenyl-substituted spirobifluorene 34 showed an emission maximum at 644 nm with a high $\Phi_{\text{film}}$ of 0.33 (Scheme 21). The choice of a dicyanoethylene moiety as an acceptor is key to the emergence of red emission (cf. 4). From X-ray analysis of its single crystal, the non-planar structure of the diphenylamino moiety and the spiro framework clearly contributes to the suppression of close-packing in the solid-state. Long-range dipole-dipole interactions may be the primary reason for fluorescence quenching. A non-doped OLED using 34 has been demonstrated to exhibit red emission ($\lambda_{\text{max}} = 638$ nm) with an external quantum efficiency of 3.6% and a maximum luminance of 11 400 cd m$^{-2}$.

Diphenylaminoisoprobifluorene-substituted fumaronitrile 35a, which can be regarded as a hybrid of 34 and the orange-red emitter 36, exhibits red PL ($\lambda_{\text{max}} = 686$ nm) with a $\Phi_{\text{film}}$ of 0.34 in the solid state (Scheme 22). Fluorine substitution at the ortho-position of the diphenyl groups (35b) induces a blue-shift of the emission maximum ($\lambda_{\text{max}} = 646$ nm) and an enhancement of $\Phi_{\text{film}}$. The donor–π-acceptor–π-donor type arrangement is key to avoiding the strong dipole that originates from the donor–π-acceptor-type electronic structure and causes severe aggregation.

Dithienylbenzothiadiazole 37a, deposited as a thin film on quartz from a CH$_2$Cl$_2$ solution, emits a red light with an emission maximum at 630 nm and a $\Phi_{\text{film}}$ of 0.39 (Scheme 23). Since 37a exhibits hole-injection and electron-transporting properties, a light-emitting device using 37a as a non-doped red emitter can operate without a hole-blocking layer. Furthermore, replacing the n-hexyl groups in 37a with 4-sec-butoxyphenyl groups enhances the glass transition temperature and solubility of the resulting derivative (37b) in toluene and xylene. A thin film, prepared by spin-coating from a toluene solution, emitted PL ($\lambda_{\text{max}} = 622$ nm) with an extremely high $\Phi_{\text{film}}$ of 0.61 as a red fluorophore. Laser emission of 37b by optical pumping has also been confirmed.

A powder of perylene tetracarboxylic acid bisimide 38 substituted by hexyl groups at the 2,5,8, and 11-positions reportedly emits a red light at 635 nm with an excellent $\Phi_{\text{powder}}$ value of 0.59 (Scheme 24). Without the hexyl groups, the...
corresponding bisimide powder was almost non-fluorescent ($\Phi_{\text{powder}} = 0.07$). In addition, the two 1-ethylpropyl groups on the nitrogen are also indispensable for the high quantum yield as changing the 1-ethylpropyl groups in 38 into 2,5-di-isopropylphenyl groups results in a non-fluorescent powder ($\Phi_{\text{powder}} = 0.02$). The introduction of alkyl groups at the 2,5,8, and 11-positions of pyrene tetracarboxylic acid bisimide was achieved by ruthenium-catalyzed C–H activation with 1-alkenes.

### 3.3. Organic Fluorophores Exhibiting Multicolor Emission by Substituent Tuning

One of the approaches for achieving white emission involves the doping of a higher-energy organic emitter (host) with a lower-energy-emitting material (guest).[70] Thus, white emission can be obtained by combining emissions from both the host and the guest. However, mixing two emitting materials may cause micro-segregation that is detrimental to the device operation if the molecular structures are largely distinct from one another. Therefore, it would be intriguing to design chromophores that are capable of exhibiting multicolor emission simply by tuning the substituents of the fixed $\pi$-conjugated main frameworks.[71] To this end, utilizing intramolecular charge transfer in a donor- and acceptor-substituted $\pi$-system is attractive because the degree of transfer that determines the emission color can be tuned from the combination of the donor and acceptor.

Use of a bithiophene moiety as a donor and a dimesitylboryl group as an acceptor with a donor–acceptor–donor type structure is remarkably effective for realizing multicolor emission with high quantum yields in thin films (Figure 7).[72] Thus, visible-light emission ranging from blue ($\lambda_{\text{max}} = 486$ nm) to red ($\lambda_{\text{max}} = 657$ nm) is achieved by appropriately choosing the terminal aryl groups of 39 as shown in Figure 7. In crystal, the bithiophene moiety is appreciably twisted with a dihedral angle of 56°, owing to substitution of the bulky boryl group at the 3-position. This twist contributes to the suppression of intermolecular interaction and the emergence of a large Stokes shifts (approx. 5290–6560 cm$^{-1}$) that is essential for retarding non-radiative intermolecular energy transfer via the Förster mechanism.

As shown in Scheme 25, unsymmetrical triarylamines 40 emit violet ($\lambda_{\text{max}} = 383$ nm) to red light ($\lambda_{\text{max}} = 631$ nm) with good to high quantum yields upon single UV excitation ($\lambda_{\text{ex}} = 343$ nm) in the solid state.[73] As the electron-withdrawing effect of the substituent R becomes greater, the emission maximum becomes increasingly red-shifted. Although the quantum yields need to be enhanced, the ease of the molecular modification of 40 is very attractive. Application of 40e in red lasers has also been demonstrated.[74]

All of the examples of efficiently fluorescent organic solids consist of multiple aromatic rings and/or polycyclic aromatic hydrocarbon skeletons. With the exception of 1,4-bis(alkenyl)-2,5-dipiperidinobenzenes 41 (Figure 8), there are no other examples of highly emissive organic solids that contain only a single benzene ring as an aromatic component.[75] The emission maxima in thin films of 41 range from

![Scheme 24. Red-emissive perylene tetracarboxylic acid bisimide.](image1)

![Figure 7. Multicolor-emissive mesitylboryl-substituted bithiophenes.](image2)

![Scheme 25. Multicolor-emissive triarylamines.](image3)
439–641 nm, in proportion to the electron-withdrawing effect of the terminal substituents at the alkenyl moieties. Substitution of dipiperidino groups at the positions ortho to the alkenyl moieties induces a distorted molecular framework in the ground state, suppressing close packing in the crystal and resulting in large Stokes shifts that lead to excellent $\Phi_{\text{f}}$ values in the solid state.

Conclusions and Perspectives

We have provided an overview of small organic fluorophores that are characterized by high quantum yields in the solid state. Most of the emissive solids are designed and developed as emitters for application in OLEDs. Although the realization of highly emissive organic solids is particularly difficult owing to concentration quenching, an inevitable phenomenon in the condensed phase, various kinds of organic fluorophores whose quantum yields exceed 0.5 for the Förster mechanism. Whilst the PL quantum yield in the solid state strongly depends on the crystalline structure and/or morphology of the aggregated structure, including the thickness of thin films, there is a clear correlation between high PL quantum yield in the solid state and excellent lumi

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