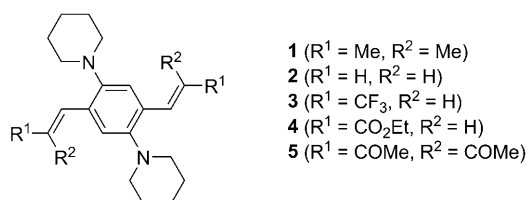


1,4-Bis(alkenyl)-2,5-dipiperidinobenzenes: Minimal Fluorophores Exhibiting Highly Efficient Emission in the Solid State**

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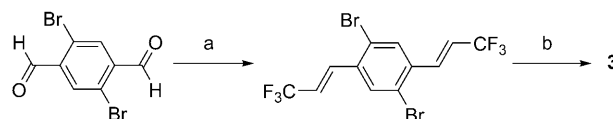
Motivated by the progress in such optoelectronic devices as organic light-emitting diodes (OLEDs),^[1] semiconductor lasers,^[2] and fluorescent sensors,^[3] scientists have paid much attention to π -conjugated compounds that emit visible light in the solid state.^[4] However, the development of organic molecules exhibiting highly efficient solid-state luminescence is an extremely challenging task because the molecular aggregation of chromophores, which is inherent in the solid state, typically results in the concentration quenching of luminescence. Therefore, examples of organic solids that exhibit intense emission with high absolute quantum yield are quite limited.^[5] The common structural feature of emissive organic solids is that they contain multiple aromatic rings and/or polycyclic aromatic hydrocarbon skeletons, which often cause problems in solubility, an undesirable property for the purification and processing of organic materials. Meanwhile, the emission colors of π -conjugated molecules are closely related to their conjugation lengths. Organic materials with good solubility have the potential of being applicable to solution processing, which is a fascinating method for the easy and low-cost fabrication of large-area optoelectronic devices. Therefore, it is intriguing to determine the minimum size of the aromatic component of highly emissive organic solids, from both fundamental and practical viewpoints.^[6] We report herein that 1,4-bis(alkenyl)-2,5-dipiperidinobenzenes **1–5**,



which contain only one benzene ring as the aromatic component, serve as novel fluorophores and emit intense visible light with high to excellent quantum yields in the solid state such as in the crystal, neat film, and doped polystyrene

film. In addition, the emission colors can be tuned in the range from blue to red simply by modifying the alkenyl moieties.

In the course of our research on the development of new synthetic methods for organofluorine compounds, we found that 2,5-dimethoxy-1,4-bis[(*E*)-3,3,3-trifluoroprop-1-enyl]-benzene in powder form showed blue fluorescence ($\lambda_{\text{em}} = 441 \text{ nm}$) with a moderate quantum yield of 0.31.^[7,8] This observation prompted us to explore this molecular/electronic structure as a minimal chromophore of emissive organic solids. Then, we prepared the corresponding counterpart **3** as a single stereoisomer from 2,5-dibromoterephthalaldehyde^[9] (Scheme 1).^[10] Benzene **3** is soluble in organic solvents such as



Scheme 1. Preparation of **3**: a) $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CF}_3$, Bu_4NF , THF, RT, and then I_2 , $h\nu$, RT, 28 %; b) piperidine, $\text{Pd}(\text{OAc})_2/(\text{S})\text{-binap}$ (cat.), NaOtBu , toluene, 100°C , 83 %. binap = 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl.

CH_2Cl_2 , CH_3CN , THF, and toluene, and it was easily purified by column chromatography on Al_2O_3 followed by recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$. Both crystals and a spin-coated thin film of **3** were found to exhibit remarkably intense green emission ($\lambda_{\text{em}} = 523$ and 526 nm) upon excitation with UV light ($\lambda = 360 \text{ nm}$) with extremely high quantum yields (Φ_{f} of 0.98 and 1.00, respectively) (Figure 1 and Table 1).^[11] Moreover, **3** dispersed in a thin film of polystyrene also emits a brilliant green light, maintaining the excellent efficiency of the solid-state emission ($\Phi_{\text{f}} = 1.00$). The absorption spectrum of **3** in cyclohexane and the fluorescence spectra ($\lambda_{\text{ex}} = 360 \text{ nm}$) in cyclohexane, CH_2Cl_2 , or CH_3CN are shown in

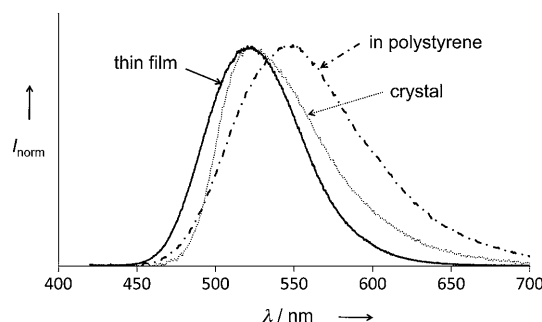


Figure 1. Fluorescence spectra of **3** in the solid states ($\lambda_{\text{ex}} = 360 \text{ nm}$).

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Table 1: Photophysical properties of **1–5**.

Cmpd	λ_{abs} [nm] ^[a] (ϵ) ^[b]	λ_{max} (Φ_f) ^[c,d]			
		solution ^[a]	crystals ^[e]	thin film ^[f]	PS film ^[g]
1	331 (4600)	439 (0.31)	441 (0.73)	439 (0.65)	439 (0.68)
2	351 (4900)	469 (0.53)	486 (0.94)	480 (0.89)	487 (1.00)
3	380 (3500)	523 (0.49)	523 (0.98)	526 (1.00)	543 (1.00)
		563 (0.57) ^[h]			
		567 (0.57) ^[i]			
4	410 (6300)	566 (0.66)	596 (0.89)	591 (0.80)	595 (1.00)
5	425 (4400)	656 (0.09)	638 (0.43)	641 (0.34)	659 (0.15)

[a] 1×10^{-5} M in cyclohexane. [b] ϵ : $\text{M}^{-1} \text{cm}^{-1}$. [c] Emission maxima upon irradiation with UV light ($\lambda_{\text{em}} = 310$ nm for **1**, 320 nm for **2**, 360 nm for **3** and **4**, 365 nm for **5**). [d] Absolute quantum yield determined with a calibrated integrating sphere system. [e] Prepared by recrystallization from mixed solvents: **1** from toluene/hexane; **2** from Et₂O/hexane; **3–5** from CH₂Cl₂/hexane. [f] Prepared by spin-coating from a solution in THF for **1** and **2**, and in toluene for **3–5**. [g] Dispersed in a polystyrene (PS) film. [h] In CH₂Cl₂. [i] In CH₃CN.

Figure 2. A large Stokes shift (142 nm) and remarkable solvatochromism of the fluorescence ($\lambda_{\text{em}} = 523$ nm in cyclohexane; 563 nm in CH₂Cl₂; 567 nm in CH₃CN) were

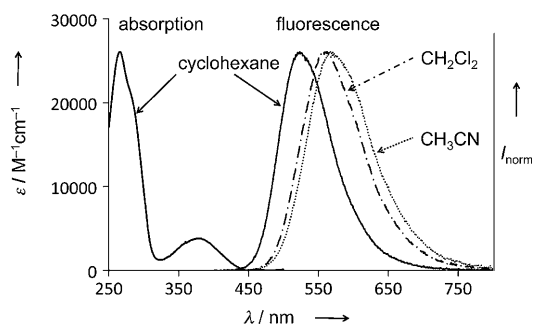


Figure 2. Absorption (left) and fluorescence spectra ($\lambda_{\text{ex}} = 360$ nm; right) of **3** in solution.

observed, suggesting significant structural differences between the ground and excited states, and solvent stabilization of the charge-transfer excited state.

Single crystals of **3** suitable for X-ray analysis were obtained by recrystallization from THF/EtOH. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with an inversion center at the centroid of the benzene ring (Figure 3).^[12] The dihedral angle between the alkenyl moiety and the benzene ring ($\angle \text{C1–C2–C3–C4}$) is 32.7° , while the piperidyl groups are more twisted out of the benzene plane ($\angle \text{C2–C5–N1–C6}$ was 72.6°). Presumably as a result of the twisted conformations of the piperidyl and the trifluoropropenyl groups, the benzene planes of the adjacent two molecules of **3** in the crystal are far away from each other (5.33 Å), and thus molecules of **3** in the crystal are prevented from intermolecular electronic inter-

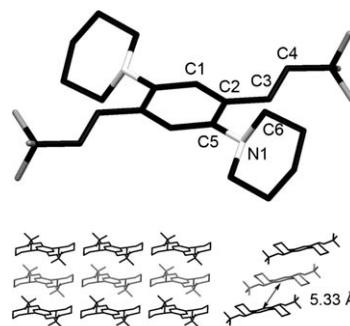


Figure 3. Molecular and crystal structures of **3**. Hydrogens are omitted for clarity.

actions, such as π – π stacking, which lead to the quenching of fluorescence.

DFT calculations (B3LYP/6-31G(d) level) of **3** disclose that the HOMO is delocalized primarily over the benzene ring and the nitrogens, and the LUMO is evident in the CF₃C=C–C₆H₄–C=CCF₃ framework (Figure 4).^[13] Moreover,

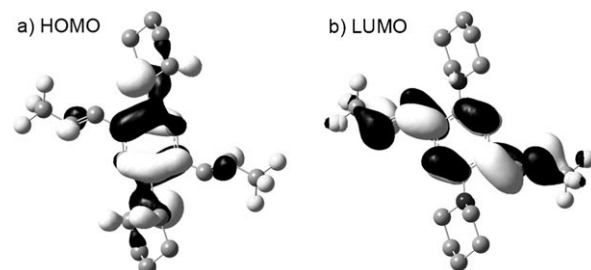


Figure 4. HOMO (a) and LUMO (b) diagrams of **3**.

the time-dependent DFT calculations indicate that the absorption band at 380 nm could be the intramolecular charge-transfer transition from the HOMO to the LUMO. This is consistent with the observed large Stokes shift and the solvatochromism.

To examine the validity of the bis(alkenyl)-dipiperidinobenzene framework as a minimal core of highly emissive organic solids, we designed and prepared **1**, **2**, **4**, and **5**, in which the terminal carbons of the alkenyl moieties were substituted with Me, H, EtO₂C, and Ac groups, respectively, in place of CF₃ groups.^[14] Their photophysical properties and the fluorescence spectra of the crystals are shown in Table 1 and Figure 5c, respectively.^[15] Bis(2-methylpropenyl) and divinyl derivatives **1** and **2** in both the crystal and the spin-coated film emit blue and greenish blue light, respectively (Figure 5a), with high to excellent quantum yields, ranging from 0.65 to 0.94. Crystals and a thin film of **4** show intense orange fluorescence ($\lambda_{\text{em}} = 596$ and 591 nm) with excellent Φ_f of 0.89 and 0.80, respectively. Moreover, diacetyl derivative **5** exhibit red fluorescence in crystals and a thin film with emission maxima at 638 and 641 nm and quantum yields of 0.43 and 0.34, respectively. Since red fluorophores typically have a tendency to aggregate in the solid state, which results in concentration quenching of fluorescence, the quantum

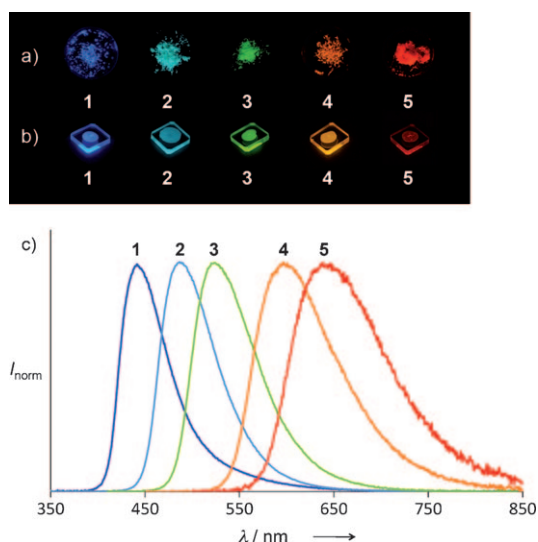


Figure 5. Photographs of a) microcrystals 1–5 and b) spin-coated polystyrene films doped with 1–5 taken under UV light ($\lambda = 365$ nm). c) Fluorescence spectra of microcrystals 1–5.

yields of solid **5**, a red emitter, are rather high.^[16] Furthermore, solids **1–4** dispersed in a polystyrene (PS) film also show strong fluorescence in colors similar to those of crystals and thin films with excellent quantum yields of 0.68 and 1.00 (Figure 5b). This behavior is quite attractive in view that the benzenes could be potential dopant emitters in host materials. It should also be noted that the Φ_f values of **1–5** in cyclohexane are much lower than those in the solid state. Thus, aggregation-induced enhanced emission is operative in all cases probably because of the restriction of intramolecular rotation.^[17] These results demonstrate that 1,4-bis(alkenyl)-2,5-dipiperidinobenzenes are unique and promising solid fluorophores in multiple colors.

In summary, we have demonstrated that 1,4-bis(alkenyl)-2,5-dipiperidinobenzenes are highly emissive fluorophores in solid states, such as crystals and thin films, and even in polystyrene film. The solid-state photoluminescent quantum yields are high to excellent, and the fluorescent color is easily tuned by modifying functional groups at the alkenyl moieties. It is of great interest from fundamental and practical viewpoints that the remarkably high efficiency of solid-state emission and the brilliant full-color emission are achieved with the compact π -conjugated system that consists of only one benzene ring as an aromatic element. These characteristics render the compact fluorophores unique and make them potential candidates for organic emitters and for applications to solid-state lighting devices. Further studies on electrochemical, thermal, and morphological properties of 1,4-bis(alkenyl)-2,5-dipiperidinobenzenes, and their applications in optoelectronic devices are in progress.

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- [13] The molecular structure was optimized by DFT methods at the B3LYP/6-31G(d) level with the crystal structure as the initial geometry.
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