Organic fluorophores that emit ultraviolet light in the aggregated state

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Abstract
Ultraviolet (UV)-emissive organic light-emitting diodes (OLEDs) have attracted growing attention as future UV-lighting sources following UV-LED. The design and development of highly efficient UV-emissive organic solids are essential for the advancement of UV-OLEDs. Reviewed herein are organic small molecules and polymers that exhibit UV emission in the aggregated state such as crystal, powder, and amorphous film. The UV-emissive molecules are in principle limited to those whose photoluminescence (PL) maxima are less than 400 nm and whose PL quantum yields in the aggregated state, which are useful for evaluating the potential of solid-state emitters, are reported. In cases that electroluminescence (EL) studies are demonstrated, the emission maxima and external quantum efficiencies with the device structures are also shown. Some exceptions are also included whose PL quantum yields are not reported, but UV-EL with an emission maximum of less than 400 nm is demonstrated.

KEYWORDS
conjugation, light-emitting materials, molecular design, solid-state emission, UV OLEDs

1 | INTRODUCTION

Since the first demonstration of organic light-emitting diodes (OLEDs) by Tang and VanSlyke in 1987,1 extensive research has been carried out on the design and development of organic luminophores that emit visible light efficiently in the solid state.2–9 The research has also contributed to the development of organic light-emitting transistors,10–13 semiconducting lasers,14–18 and luminescent biological and chemical sensors (Scheme 1).19–24 In sharp contrast, the exploration of ultraviolet (UV)-emissive organic materials whose solid-state emission maxima are < 400 nm is far behind. However, stimulated by the technological advance of UV-LEDs for applications in high-density data recording,25 lithography,26 security,27 sensing,28 sterilization,29 UV curing,30 vegetable plant31 and water purification32–34 growing interest has recently been paid to the development and applications of organic luminophores that exhibit UV emission in the aggregated state.35,36

To develop UV-emissive organic materials, it is essential to design π-conjugated compounds whose effective conjugation lengths are shorter than those of violet-emissive luminophores. Hence, compact π-conjugated modules such as oligophenyls, oligofluorenes, phenanthrene, and silicon-bridged biaryls are commonly appropriate as the core of organic UV emitters. It is, however, unfavorable to incorporate strong electron-donating and -accepting groups, which are generally beneficial for OLED applications, simultaneously into such compact luminescent modules. This is because efficient intramolecular charge transfer (ICT) from the donor to the acceptor causes a bathochromic shift of a luminescence spectrum to the visible region. As host materials used in OLEDs should have deeper HOMO and higher LUMO levels than those of visible-light-emitting dopant materials, respectively,37–39 host materials suitable for blue OLEDs have the potential as UV emitters. This review article focuses on organic luminophores that fluoresce in the aggregated state such as crystal, powder, and amorphous film with a photoluminescence (PL) maximum of less than 400 nm and whose PL quantum yield in the aggregated state is available in the original literature. Some exceptions that are demonstrated to exhibit UV electroluminescence (EL) with an emission maximum of less than 400 nm without showing their PL quantum yields are also included. In the light of the aim and scope of Aggregate, the photophysical properties of UV-emitter-doped films are excluded except for a TADF-type UV emitter. The UV emitters are classified into the following compound classes: oligophenyls, oligofluorenes,
phenanthrenes, and N-heterocycles such as oxadiazoles, triazoles, purine, and carbazoles, silicon-containing compounds such as silicon-bridged biaryls and disilanes, dialkenyl-dialkoxybenzenes, and polymers (Scheme 2).

The following conventional abbreviations are used for typical hole- and electron-transporting (host) materials:

- BCP: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
- BCP: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
- BPhen: 4,7-diphenyl-1,10-phenanthroline
- Bu-PBD: 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole
- CBP: 4,4′-bis(9-carbazolyl)-2,2′-biphenyl
- CuPc: copper phthalocyanine
- FIrpic: bis[2-(4,6-difluorophenyl)pyridinato-C2,N](picolinato)iridium(III)
- HAT-CN: 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile
- ITO: indium tin oxide
- Ir(mppy)3: tris[2-(p-tolyl)pyridine]iridium(III)
- Liq: 8-hydroxyquinolinolatinilithium
- mCP: 1,3-bis(N-carbazolyl)benzene
- PBD: 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole
- PEDOT: poly(3,4-ethylenedioxythiophene)
- PSS: polystyrene sulfonate
- PTOPT: poly[3-(4-octylphenyl)-2,2′-bithiophene]
- PVK: poly(N-vinyl carbazole)
- TACP: 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane
- TAZ: 3-(4-biphenyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole
- TCTA: 4,4′,4″-tris(N-carbazolyl)triphenylamine
- Tm3PyP26PyB: 1,3,5-tris-6-[3-(pyridine-3-yl)phenyl]pyridin-2-yl]benzene
- TPBI: 2,2′,2″-(1,3,5-benzenetriyl)tris(1-phenyl-1H-benzimidazole)
- TPD: N,N′-bis(3-methylphenyl)-N,N′-diphenylbenzidine
- UGH2: 1,4-bis(triphenylsilyl)benzene

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2.1 | Oligophenyls

Terphenyl (1) and p-quaterphenyl (3) in vacuum-deposited neat film showed fluorescence spectra with vibronic structure, in which the strongest emission maxima were at 370 and 388 nm, respectively (Figure 1, Table 1), although the fluorescence quantum yields were low (0.13 for 1 and 0.07 for 3).[40] When the terminal phenyl rings of 1 and 3 were replaced by 1-naphthyl groups, the resulting oligoaryls 2 and 4 exhibited UV fluorescence at 379 and 384 nm, respectively, with higher quantum yields (0.22 for 2 and 0.31 for 4). The X-ray diffraction study of the films disclosed that 1 and 3 were in a polycrystalline state, while 2 and 4 were in the amorphous state. Hence, it is assumed that di-substitution of 1-naphthyl groups on benzene and biphenyl weakens the intermolecular interactions such as π–π stacking and thus contributes to the suppression of luminescence quenching. The higher fluorescence quantum yields and amorphous behavior of neat thin films of 2 and 4 led to the emergence of amplified spontaneous emission (ASE). ASE is luminescence produced by optical pumping of organic laser dyes in a light gain medium and ASE-active materials are expected as light sources emitting superluminescent radiation.[14] No ASE was observed with 1 and 3. The narrowed emission bands of 2 and 4 appeared at 385 and 391 nm, respectively, with full widths at half...
maximum (FWHM) of about 10 nm each. The ASE thresholds were about 0.14 mJ/cm², which was lower than that (0.23 mJ/cm²) of p-sexiphenyl. These results demonstrated a potential of naphthyl-terminated oligophenyls as laser materials.

A vacuum-deposited thin film of CBP (5), which is one of the standard hole-transporting host materials for OLEDs, showed fluorescence with an emission maximum at 390 nm with a high quantum yield of 0.61 (Figure 1, Table 1). [41] As N,N,N′,N′-tetraphenylbenzidine, TPD, 4,4′-bis(3-methylcarbazol-9-yl)-2,2′-biphenyl, and 4,4′-bis(3,6-dimethylcarbazol-9-yl)-2,2′-biphenyl in film efficiently fluoresced at 419, 424, 400, and 409 nm with high quantum yields of 0.44, 0.41, 0.49, and 0.60, respectively. [41] ASE of 5 was observed at 394 nm with a low threshold of 1.3 ± 0.2 μJ/cm² and a very narrow FWHM (4.3 nm). UV EL was demonstrated at 390 nm with a device composed of ITO/CuPc/5/Bu-PBD/CsF/Al. [42] The external quantum efficiency (EQE) was 1.25%, which was attained by thickness optimization of CuPc and Bu-PBD layers. Fabrication of microcavity OLEDs using 5 and their application to oxygen sensing were also reported. [43]

A vacuum-deposited film of 4,4′-bis(diphenylphosphine oxide)biphenyl (6), a wide bandgap electron-transporting material, exhibited PL with an emission maximum at 332 nm, although the quantum yield has not been reported (Figure 1, Table 1). [44] EL spectra of ITO/CuPc/6/LiF/Al devices showed emission maxima in the UV region ranging from 330 to 350 nm depending on the layer thickness of 6. The EQEs of the devices, in which 6 acted as a UV-emitter, were very low (0.008%–0.044%), while when 6 was used as a host material for Irpic, a standard blue electrophosphor, [45] an EQE of the blue-emissive device reached 7.8%.

Quaterphenyl 7 in vacuum-deposited film fluoresced at 363 nm with an excellent quantum yield of 0.86 (Figure 1, Table 1). [46] The central biphenyl moiety of 7 in crystal-adopted planar conformation, while the terminal phenyl rings were twisted due to the acetal bridge by about 40° with respect to the biphenyl plane, resulting in the shorter wavelength of emission. As no π–π intermolecular interaction was observed and the acetal bridges restricted the intramolecular motion, the efficient solid-state UV emission is probably originated from the bridged and twisted molecular structure. EL spectrum of a device fabricated as ITO/PEDOT/7/Ba/Al showed an emission maximum at 372 nm with a maximum luminance of 11 cd/m² and current efficiency of 0.07 cd/A.

### 2.2 Oligofluorenes

Various types of oligofluorenes, including their spiro derivatives, have been developed as solid-state UV emitters. In particular, spirobifluorene structures are beneficial for imparting amorphous nature and suppressing intermolecular electronic communications resulting in luminescence quenching. [47] Diphenylspirobifluorene 8 that forms a vitreous amorphous film showed a vibronic structured fluorescence spectrum with an emission maximum at 387 nm (Figure 2, Table 2). [48] The amorphous film prepared by spin-coating exhibited ASE at 381 nm with a minimum threshold of 0.5 μJ/cm². The application of the amorphous thin-film to distributor feedback lasers was also demonstrated.

Naphthyl-substituted spirobifluorenes 9 and 10 in vacuum-deposited amorphous film fluoresced at 399 and 381 nm, respectively (Figure 2, Table 2). [49,50] The glass transition temperatures (Tg) of 9 and 10 were 99 and 103°C,
**Figure 2** Molecular structures of 8–16

**Table 2** Luminescence data of 8–16

| Compound | 8    | 9    | 10   | 11   | 12a  | 12b  |
|----------|------|------|------|------|------|------|
| \(\lambda_{\text{PL}}\) (nm) | 387 (NR) | 399 (385) | 381 (382) | 392 (392) | 392 (402) | 392 (396) |
| \(\Phi\) (EQE) | NR (NR) | NR (2.9) | 0.70 (2.2) | 0.66 (3.6) | 0.63 (2.8) | 0.57 (2.7) |

| Compound | 13a  | 13b  | 14   | 15   | 16   |
|----------|------|------|------|------|------|
| \(\lambda_{\text{PL}}\) (nm) | 392 (393) | 393 (393) | 394 (402) | 369 (388) | 392 (395) |
| \(\Phi\) (EQE) | 0.56 (2.6) | 0.60 (3.1) | 0.92 (0.2) | NR (1.6) | NR (2.1) |

Note: \(\lambda_{\text{PL}}\): wavelength of PL maximum, \(\lambda_{\text{EL}}\): wavelength of EL maximum, \(\Phi\): fluorescence quantum yield. Abbreviations: EQE, external quantum efficiency (%); NR, not reported.

respectively, indicating that their morphological stabilities are good. Using device structures of ITO/PEDOT: PSS/PVK/9 or 10/PBD/LiF/Al, 9 and 10 exhibited UV-EL at 385 and 382 nm with EQEs of 2.9% and 2.2%, respectively.

Direct connection of 9,9-diarylfuorenes is an effective molecular design of UV-luminophores that exhibit high thermal and morphological stabilities and high fluorescence quantum yields in the solid state. Bi(spirobifluorene) 11 and bi(9,9-diarylfuorene)s 12a and 12b, which exhibited high decomposition temperatures \((T_d: 382 \degree C\) for 11, 385 \degree C for 12a, and 424 \degree C for 12b) and \(T_g\)s \((174 \degree C\) for 11, 153 \degree C for 12a, 169 \degree C for 12b), showed UV fluorescence in vacuum-deposited amorphous film at 392 nm with excellent quantum yields (Figure 2, Table 2).\(^{[51]}\) The UV emission was originated from the quaterphenyl backbones and the planar structure of a fluorene moiety made the excited state stable. The diaryl groups substituted at 9-positions of the fluorene units inhibited the dense packing, which should cause luminescence quenching via intermolecular electronic interactions, and contributed to the achievement of the excellent thermal and morphological stabilities. Highly efficient UV-EL of 11, 12a, and 12b were also demonstrated with a device architecture of ITO/PEDOT: PSS/TCTA/11 or 12/TPBI/LiF/Al, respectively.

Difluorenylated spirobifluorenes 13a and 13b in thin film were also developed as UV emitters (Figure 2, Table 2).\(^{[52]}\) The \(T_g\) values of 13a and 13b were 464 and 475 \degree C, respectively, which were much higher than those of 12a and 12b probably due to the molecular size (weight). The \(T_g\) values of 13a and 13b were also superior to those of 12a and 12b. The emission maxima and fluorescence quantum yields of 13a and 13b in thin film were almost similar with those of 11 and 12 in the thin film. UV-EL was observed with the same device structure used for 11 and 12 and the EQE (3.1%) of the 13b-embedded device was the highest among the devices using 11–13. Remarkably, 13a and 13b were demonstrated to serve as host materials for red phosphorescent OLEDs.

Bis(spirobifluorenyl)-substituted diphenylsulfone 14 exhibited highly efficient UV fluorescence at 394 nm in amorphous neat film with a quantum yield of 0.92 (Figure 2, Table 2).\(^{[53]}\) An OLED whose configuration was ITO/PEDOT:PSS/14/TPBI/Cs2CO3/Al showed a slightly redshifted EL at 402 nm compared with the PL with an EQE of 0.2%. Although the value of the EQE was low, it is noteworthy that a non-doped UV OLED was achieved. In addition, the triplet energy was estimated by phosphorescence
in CH$_2$Cl$_2$ at 77 K as 2.85 eV, which is higher than those of Flrpic (2.62 eV) and Ir(mppy)$_3$ (2.55 eV), suggesting that 14 can act as a host material for blue and green OLEDs. Indeed, Flrpic and Ir(mppy)$_3$-doped OLEDs whose configuration was the same as the UV OLED showed efficient EL with emission maxima at 472 and 514 nm and EQEs of 6.8% and 8.8%, respectively.

Vacuum-deposited neat films of bis- and tris(spirobifluorenyl)benzenes 15 and 16 exhibited PL at 369 and 392 nm, respectively (Figure 2, Table 2). This implies that linking multiple spirobifluorenyl moieties with a benzene ring spacer was also effective for attaining UV fluorescence, whose emission maxima are less than 400 nm and excellent morphological stability ($T_g$: 183 °C for 15 and 237 °C for 16). UV-EL of 15 and 16 appeared at 388 and 395 nm with EQEs of 1.6% and 2.1%, respectively, with a device configuration of ITO/PEDOT:PVK/15 or 16/PBD/LiF/Al.

2.3 Phenanthrenes

Benzofuranyl-, benzo thiophenyl-, bis(benzofuranyl)-, and dibenzofuranyl-substituted phenanthrenes 17–20 emitted UV light at 361–395 nm in the aggregated state formed in a 1:1 mixture of DMF and water (Figure 3). The fluorescence quantum yields of 17–19 in the aggregated state were good-to-excellent (0.90 for 17, 0.79 for 18, and 0.47 for 19) and much higher than those (0.62 for 17, 0.65 for 18, and 0.37 for 19) in DMF solution, indicating that 17–19 exhibited aggregation-induced emission enhancement. In contrast, the quantum yield of the aggregated 20 was 0.25, which was lower than that (0.42) in DMF, implying that 20 experienced aggregation-caused quenching. Non-doped OLED using 19 as an emitting layer showed UV emission at 383 nm with a device structure of ITO/CBP/19/BCP/LiF/Al, although the EQE was not reported.

2.4 N-Heterocycles

Efficient UV-OLED was fabricated using TAZ (21), which is one of the typical electron-transporting materials, as a light-emitting layer (Figure 4, Table 4). The EL device consisting of ITO/PEDOT:PSS/CBP/21/BCP/LiF/Al exhibited UV emission at 380 nm with EQE of 4.1% and FWHM of 42 nm. The white emission whose Commission Internationale de l’Eclairage (CIE) coordinates were (0.33, 0.31) was realized with an EQE of 1.1% by combining the UV-emissive device and red, green, and blue color conversion materials. The higher EQE (4.6%) and narrower FWHM (35 nm) of 21-based UV-OLED were achieved by an ITO/PEDOT:PSS/MoO$_3$/CBP/21/BPhen/LiF/Al device, in which the use of double-stacked hole-injection layer was essential for the improvement of the performances.

A vacuum-deposited thin film of 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (22), which is another standard electron-transporting material and generally abbreviated as PBD, fluoresced at 390 nm (Figure 4, Table 4). An ITO/PTOPT:22/Ca/Al device emitted UV at 394 nm with an EQE of 0.1%.[59] Since no EL was observed with an ITO/Ca/Al device, PTOPT was essential for the UV–EL and was considered to function as a hole-injecting material in the device. Application of 22 to a host material for fluorescent laser dyes such as coumarin 490, DCMII, and LDS821 was also demonstrated.

The third example of UV-emissive electron-transporting materials is OXD-7 (23) (Figure 4).[61,62] EL at 388 nm with an EQE of 1.43% was achieved with a device structure of ITO/MoO$_3$/CBP/23/LiF/Al (Table 4). The insertion of a MoO$_3$ layer as hole injection and buffer material between the ITO electrode and the CBP layer is essential for the UV emission. When the MoO$_3$ layer was absent, the emission maximum was redshifted to 408 nm and the EQE dropped to 0.98%.

Purine derivative 24 exhibited UV fluorescence at 393 nm with a quantum yield exceeding 0.95 in CH$_2$Cl$_2$, whereas an emission maximum of 24 in neat film significantly redshifted to around 470 nm (Figure 4, Table 4).[63] These results suggest that 24 cannot apply to non-doped UV OLEDs, but can be used as a UV dopant. In fact, UV–EL with emission maximum and EQE of 393 nm and 1.6%, respectively, was achieved with a multilayer device whose architecture was ITO/TAPC/mCP:24/UGH2/OXD-7/LiF/Al.

A vacuum-deposited thin film of 1,2-diphenyl-1H-phenanthro[9,10-d]imidazole (25a) fluoresced at 395 nm with a quantum yield of 0.40 (Figure 4, Table 4). The EL spectrum of 25a in a multilayer device (ITO/MoO$_3$/NPB/TCTA/25a/TPBI/LiF/Al) was redshifted by 17 nm compared with that of PL, resulting in visible light emission. On the other hand, dimethylated derivative of 25a,
thus 25b, exhibited UV–EL with emission maxima at 378 and 392 nm with an excellent EQE of 5.4% in a multilayer device architecture of ITO/MoO\textsubscript{3}/TCTA/CBP/25b/TPBI/LiF/Al.\cite{65} Notably, very narrowband UV emission was realized with an FWHM of 9.95 nm by fabricating microcavity OLEDs of 25b. N-Ethyl-1,3,6,8-tetraphenylcarbazole (26) in thin film exhibited UV emission at 391 nm whose spectrum was almost overlapped with that in CHCl\textsubscript{3} solution, suggesting that there was no intermolecular electronic interaction between each 26 in the solid state (Figure 4, Table 4).\cite{66} A non-doped OLED consisting of ITO/MoO\textsubscript{3}/26/TPBI/Alq\textsubscript{3}/LiF/Al exhibited EL at 394 nm with an EQE of 2.1%.

Organic luminophores that exhibit thermally activated delayed fluorescence (TADF) in the visible region have been extensively developed as the third generation of light-emitting materials for OLEDs, because the internal quantum efficiency of TADF-based OLEDs can be up to 100% without the aid of precious metals such as iridium and platinum.\cite{67–73} In contrast, the development of UV-emissive TADF materials remains unexplored. In 2020, dimethylmethylene-bridged diaryl sulfone 27 emerged as the first example (Figure 4).\cite{74} The fluorescence maximum, quantum yield, and lifetimes of 27 in a thin film of 9-(4-tert-butylphenyl)-3,6-bis(triphenylsilyl)-9H-carbazole (CzSi) were 392 nm, 0.46, and 3.73 ns for prompt fluorescence and 4.85 ns for delayed fluorescence, respectively. A double-emissive layer-structured OLED device of ITO/HAT-CN/HAT-CN:TAPC/TCTA:27/CzSi:27/Tm3PyP26PyB/LiF/Al emitted UV light at 389 nm with an EQE of 9.3%, which is the highest efficiency among UV-OLEDs reported so far. As the corresponding unbridged diaryl sulfone, which was developed by Adachi and coworkers in 2012, exhibited efficient blue-TADF,\cite{75} the dimethylmethylene bridge contributed to the enlargement of the HOMO–LUMO gap, resulting in TADF in the UV region.

### 2.5 Silicon-containing compounds

Silicon-bridged biaryls have found many applications as functional organic materials such as electron-transporting, light-emitting, semiconducting, and sensing materials.\cite{76–81} Organic fluorophores that emit UV light in the aggregated state are no exception. Simple silafluorenes 28 in microcrystal fluoresced in the UV region ranging from 345 to 351 nm (Figure 5).\cite{82} As listed in Table 5, the bulkier the substituents, the higher the quantum yields, and the highest value (0.33) was observed with tert-butylphenylsilylene derivative 28d. The relationship between the bulkiness of the substituents and the quantum yields may be understandable by assuming that the bulkier substituents inhibit close packing more efficiently than less bulky ones, resulting in lower loss of the excited energy. A spin-coated thin film of 2,7-diphenylated silafluorene 29 emitted UV light at 379 nm with a high quantum yield of 0.65.\cite{83} Cyclic siloxane 30 containing two silafluorene moieties in powder also exhibited efficient UV emission (λ\textsubscript{em} = 377 nm, Φ = 0.54).\cite{84} As the quantum yield of 30 in THF was 0.15, the solid-state emission was induced by aggregation. Dimethylsilylene-bridged silafluorenes 31a and 31b in spin-coated film showed fluorescence at 361 and 397 nm, respectively. These results indicate that the second silylene bridge extended the silafluorene-based π-conjugated systems. Density functional theory (DFT) calculations disclosed that the extension was ascribed to the effective σ*-π* conjugation between the σ* orbital of the exocyclic Si–Me bonds and the π* orbital of the silafluorene fragment.\cite{76} Vacuum-deposited amorphous film of spirosilabifluorene 32 exhibited UV luminescence at...
TABLE 5  Luminescence data of 28–40

| Compound | 28a | 28b | 28c | 28d | 29 | 30 |
|----------|-----|-----|-----|-----|----|----|
| \( \lambda_{PL} \) (nm) | 349 | 347 | 351 | 345 | 379 | 377 |
| \( \Phi \) | 0.11 | 0.25 | 0.18 | 0.33 | 0.65 | 0.54 |

| Compound | 31a | 31b | 32 | 33 | 34 | 35 |
|----------|-----|-----|----|----|----|----|
| \( \lambda_{PL} \) (nm) | 361 | 397 | 398 | 396 | 395 | 366 |
| \( \Phi \) | 0.11 | 0.17 | 0.44 | 0.70 | 0.51 | 0.08 |

| Compound | 36 | 37 | 38 | 39 | 40a | 40b |
|----------|----|----|----|----|-----|-----|
| \( \lambda_{PL} \) (nm) | 329 | 362 | 390 | 395 | 391 | 385 |
| \( \Phi \) | 0.04 | 0.02 | 0.12 | 0.07 | 0.11 | 0.44 |

Note: \( \lambda_{PL} \): wavelength of PL maximum, \( \Phi \): fluorescence quantum yield.

398 nm with a quantum yield of 0.44.\(^{[85]}\) Due to the spiro and asymmetric form, the thin film was morphologically very stable (\( T_g = 203 \) °C). Replacing the peripheral phenyl groups by 2-pyridyl and biphenyl caused a red-shift of luminescence, resulting in blue emission. Highly efficient UV fluorescence was attained with fused silafluorenes 33 and 34 in microcrystals with quantum yields of 0.70 and 0.51, respectively.\(^{[86]}\) X-ray diffraction analysis of their single crystals disclosed that the pentacyclic skeletons were completely and almost flat, respectively, with an orthogonal arrangement of the isopropyl groups to the planes, an ideal conformation for \( \sigma^*–\pi^* \) conjugation. Each molecule in the crystal was well separated from one another and had no \( \pi–\pi \) stacking in the crystalline state, resulting in the efficient solid-state fluorescence.

In addition to silafluorenes, namely silicon-bridged biphenyls, silicon-bridged phenylheteroles 35–39 emitted UV light in microcrystals, although the quantum yields were low (Figure 5, Table 5).\(^{[86]}\) This was probably ascribed to the heavy atom effect of sulfur, which causes intersystem crossing from the lowest singlet excited state to the triplet excited states. Indeed, intense green phosphorescence of 37 in 2-methyltetrahydrofuran was observed at 77 K. The wavelength of an emission maximum (329 nm) of 36 was much shorter than that (366 nm) of 35 due to the cross-conjugated molecular framework. Aryldisilanyl groups-substituted thiophenes 40a (R = CN) in amorphous powder and 40b (R = CO\(_2\)Et) in microcrystalline powder also showed UV fluorescence at 391 and 385 nm with quantum yields of 0.11 and 0.44, respectively.\(^{[87]}\) DFT calculations of 40b revealed that the HOMO was mainly developed on the thiophene ring and disilanyl moieties and the LUMO was localized on the ethoxycarbonyl-substituted benzene rings, and the HOMO–LUMO transition involved ICT from the Si–Si–thiophene–Si–Si moiety to the terminal phenyl groups.

2.6 Dialkenyldialkoxybenzenes

We have recently demonstrated that 2,5-dialkoxy- and 2,5-dilxyloxy-1,4-dialkenybenzenes 41–45 acted as efficient UV emitters (Figure 6).\(^{[88]}\) The fluorescence maxima in the solid state can be altered in the range between 336 and 385 nm (Table 6). The wavelengths of emission maxima (352 and 336 nm) of 41a and 41b were significantly blushedifted compared with those (365–380 nm) of 42, because the substitution of methyl groups at 1-positions of the alkenyl moieties induced more twisted conformations, widening the HOMO–LUMO gaps compared with those of unmethylated counterparts. Replacing the alkoxy groups by the siloxy groups...
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Table 6: Luminescence data of 41–45

| Compound | 41a | 41b | 42a | 42b | 42c | 43a |
|----------|-----|-----|-----|-----|-----|-----|
| λ\text{PL} (nm) | 352 | 336 | 380 | 380 | 365 | 371 |
| Φ          | 0.20 | 0.06 | 0.40 | 0.31 | 0.33 | 0.44 |

| Compound | 43b | 43c | 43d | 43e | 44 | 45 |
|----------|-----|-----|-----|-----|----|----|
| λ\text{em} (nm) | 383 | 385 | 369 | 376 | 374 | 385 |
| Φ          | 0.55 | 0.55 | 0.40 | 0.41 | 0.40 | 0.45 |

Note: λ\text{PL}: wavelength of PL maximum, Φ: fluorescence quantum yield.

Also resulted in a hypochromic shift of the maxima. The fluorescence quantum yields were good-to-high (0.31–0.55) except for 41. In particular, when adamantylidene groups were used as the alkanyl moieties, UV emission was efficient irrespective of whether the molecular structure was C₃ symmetric (43) or not (44 and 45). DFT calculations revealed that the dialkenylidemethoxybenzenes were optically excited via weak ICT from the ether oxygen atoms to the twisted alkanyl–benzene–alkenyl moiety, whereas the optical excitation of the dialkenylidemethoxybenzenes involved weak ICT from the twisted π-conjugated skeleton with the oxygen atoms to the phenyl–Si moieties of each triphenylsilyl group. The latter case demonstrates the first example of a Ph–Si moiety functioning as an electron-acceptor for ICT.

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Polymerization of luminescent monomers generally causes the extension of effective conjugation length compared with that of the monomer. Hence, to keep the effective conjugation length short enough to emit UV light, it is essential to incorporate sp³ carbon/silicon atoms into the polymer main chain, connect the UV-emissive monomers with meta-linkage, or both. The first example of UV-emissive polymers is poly(m-phenylenes) 46 that fluoresced at 345 nm in film (Figure 7, Table 7).

El of 46 was investigated with ITO/PEDOT: PSS/46/OXD-7 or TAZ/LiF/Al devices. However, the observed emission was originated from the electron-transporting materials (ETMs) and the exciplexes formed between 46 and the ETMs. The realization of UV-OLED that uses 46 as an emitting layer requires an ETM with a LUMO higher than that of 46.

Efficient UV emission was demonstrated with fluorene-based nonconjugated polymers 47–49 (Figure 7, Table 7). A spin-coated thin film of 47 showed UV fluorescence with an emission maximum at 395 nm accompanying a shoulder at 415 nm and a high quantum yield of 0.56. EL spectrum of a device fabricated as ITO/PEDOT: PSS/47/TPBI/CsF/Al exhibited UV emission at 397 nm with an EQE of 1.1%. The EQE was improved up to 1.8% without changing the emission maximum wavelength by doping 47 in PVK in a weight ratio of 98:2. Efficient UV fluorescence was also observed with spin-coated thin films of polymers 48 and 49, which consisted of fluorene and tetraarylsilane moieties, with quantum yields of 0.56 and 0.47, respectively. The PL spectra showed maxima at 397 and 396 nm, respectively, that were quite similar, indicating that the slight modification of tetraarylsilane moieties has little effect on the PL properties. EL spectra of ITO/PEDOT: PSS/48 or 49/TPBI/CsF/Al devices were similar to those of the PL spectra, respectively. No obvious emission was observed in the 500–600 nm range, where the emission from the aggregates and/or ketonic defects of polyfluorenes generally appears. This result suggests that tetraarylsilane moieties not only interrupt the π-conjugation of the polymer chain but also improve the thermal and color stabilities of the resulting polymers.

Twisted biphenyl moieties-containing polymer 50 was one of the examples where meta-linkage was adopted for keeping PL of conjugated polymers in the UV region (Figure 7).

The fluorescence maximum and quantum yield in spin-coated film were 397 nm and 0.15, which were much redshifted compared with that (368 nm) in THF and lower than the value of 0.62 in THF, respectively. These results suggest that serious interchain interactions that caused luminescence quenching have occurred in the aggregated state. EL performances were also reported with a device consisting of ITO/PEDOT: PSS/50/Ba/Al.

Poly(9,9′-dihexyl-3,6-silafluorene) (51) in spin-coated film emitted UV light at 360 nm (Figure 7). As a thin film of poly(9,9′-dihexyl-2,7-silafluorene) exhibited efficient blue fluorescence at 425 nm, the UV emission is attributed to the meta-linkage of silafluorene units.

A spin-coated thin film of poly(9-butyldiphenylsilane) (52) exhibited UV emission at 357 nm with FWHM of 19 nm (Figure 7). The narrow PL band is originated from the radiative decay from the S₁ state generated by the excitation of σ-electrons of the silicon–silicon σ-bonds to the σ* orbital.

The device structure of ITO/PEDOT: PSS/52/Ca/Al showed an EL spectrum consisting of a sharp UV band at 357 nm that was consistent with the PL and a broad and intense band in the visible region. Thanks to the broad visible-light emission, the emission color of the EL device was nearly white with CIE coordinates of (0.36, 0.35). Since silicon–silicon σ-bonds are cleaved by UV irradiation,
there is concern that degradation of polysilanes may occur during OLED operation.

Poly(pyridinium salt) 53, which exhibited lyotropic liquid-crystalline properties in polar organic solvents such as acetonitrile, dimethyl sulfoxide, and methanol, showed fluorescence at 390 nm in spin-coated film (Figure 7, Table 7).[99]

4 | CONCLUSION

We have reviewed the current status of organic UV emitters with PL maxima and fluorescence quantum yields in the aggregated states such as crystal, powder, and amorphous film. UV emitters, which are demonstrated to exhibit UV-EL at < 400 nm with no data on PL, are also included. As less attention has been paid to UV-emissive organic luminophores so far, the structural variation of the UV emitters is quite limited (Scheme 1). This means that there is much room for the exploration and creation of novel organic UV emitters. Figure 8A,B shows plots of the PL maxima versus fluorescence quantum yields and EL maxima versus EQEs, respectively. As can be seen in Figure 8A, the shortest wavelength of the PL maximum was 329 nm of 36, and the highest PL quantum yield (0.94) was attained with 14. All of the data spots except for 7, 21, and 28d are located below an auxiliary line that penetrates the data spots of 14 and 36. Thus, the shorter the emission maxima, the lower the PL quantum yields. Therefore, it is a challenge to develop novel organic UV emitters that can plot their performances above the auxiliary line. In addition, the UV emitters that were applied to OLED are very limited (Figure 8B). Noteworthy is that an OLED device using 27 achieved the excellent EQE of

**FIGURE 7** Molecular structures of 46–53

**TABLE 7** Luminescence data of 46–53

| Compound | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 |
|----------|----|----|----|----|----|----|----|----|
| $\lambda_{PL} (\lambda_{EL})$ (nm) | 345 | 395 (397) | 397 (398) | 396 (396) | 397 (395) | 360 | 357 (357) | 390 |
| $\Phi$ (EQE) | NR | 0.56 (1.1) | 0.56 (1.6) | 0.47 (0.3) | 0.15 (0.05) | NR | NR (0.01) | NR |

Note: $\lambda_{PL}$: wavelength of PL maximum, $\lambda_{EL}$: wavelength of EL maximum, $\Phi$: fluorescence quantum yield.

Abbreviations: EQE, external quantum efficiency (%); NR, not reported.
9.3% with the aid of TADF. This result clearly shows one of the directions for the development of UV emitters whose EQEs exceed over 5%. In addition to efficient solid-state fluorescence, organic luminophores that apply to OLED should exhibit high thermal and morphological stabilities and good charge-accepting/transporting properties. Then, it is also necessary to establish molecular design principles that impart charge-accepting/transporting properties. Then, it is also necessary to establish molecular design principles that impart charge-accepting/transporting properties.

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