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High Fluorescence Efficiencies and Large Stokes Shifts of Folded Fluorophores Consisting of a Pair of Alkenyl-Tethered, *π*-Stacked Oligo-*p*-phenylenes

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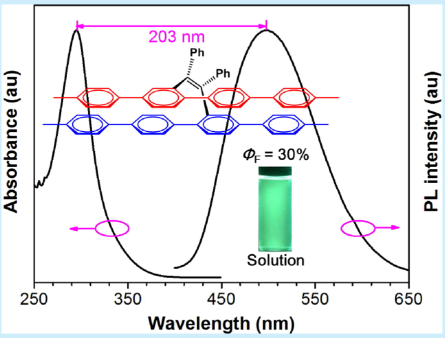
Ⓢ *Supporting Information*

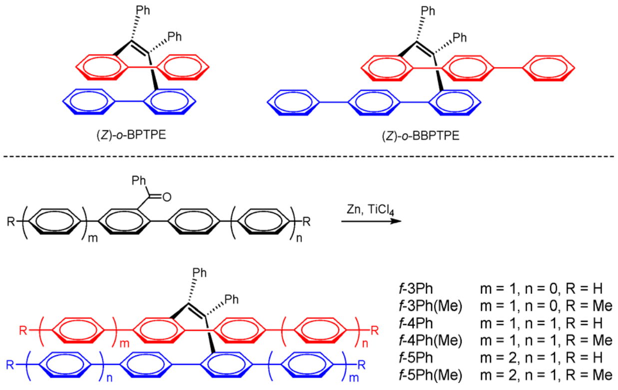
ABSTRACT: A series of pure hydrocarbon fluorophores containing a pair of *π*-stacked oligo-*p*-phenylenes have been synthesized and analyzed by NMR and X-ray crystallography. They show good fluorescence in solutions and enhanced fluorescence in the aggregated state. Large Stokes shifts (up to 214 nm) have been achieved in these folded fluorophores in virtue of intramolecular energy transfer, and balanced structural rigidity and flexibility. These folded fluorophores provide perfect models for understanding the energy and charge transfer process in *π*-stacked systems.



High fluorescence efficiency and large Stokes shifts are important parameters for fluorescent dyes, and large Stokes shifts are highly preferred to diminish self-absorption and light scattering in optical materials, such as fluorescent probes,[1] organic light-emitting diodes,[2] organic lasers,[3] etc. However, in most cases, high fluorescence efficiency and large Stokes shifts are not compatible, especially for conventional dyes, such as BODIPY,[4] coumarin,[5] rhodamine,[6] and fluorescein.[7] They show strong fluorescence in dilute solutions but become weakly fluorescent in concentrated solutions or in the solid state, which is partially caused by the severe self-absorption among closely located dye molecules due to their intrinsic small Stokes shifts.

The trials of enlarging Stokes shifts are always present, commonly by virtue of intramolecular charge/proton transfer or excimer/exciplex formation.[8] However, these approaches cannot fully meet practical demands in many cases, exhibiting variations that are difficult to control. For example, excited state intramolecular proton transfer (ESIPT) is often accompanied by a large Stokes shift but is highly sensitive to surrounding conditions, such as pH or solvent.[9] Strong intramolecular charge transfer (ICT) in high-polar media can prolong the Stokes shifts but can also drastically depress the fluorescence.[10] Therefore, it remains a challenging task to prepare fluorophores with both high fluorescence efficiencies and large Stokes shifts, particularly pure hydrocarbon systems containing no heteroatoms to function in ESIPT and ICT. To address this issue, we elaborate a series of folded pure hydrocarbon fluorophores comprising a pair of alkenyl-bridged, *π*-stacked oligo-*p*-phenylenes. Large Stokes shifts and high fluorescence efficiencies are attained in these fluorophores. By conducting a comparative study on individual oligo-*p*-phenylenes and the folded archetypes, (*Z*)-*o*-BPTPE and (*Z*)-*o*-BBPTPE (Scheme 1), the intramolecular

Scheme 1. Chemical Structures and Syntheses of the Folded Fluorophores



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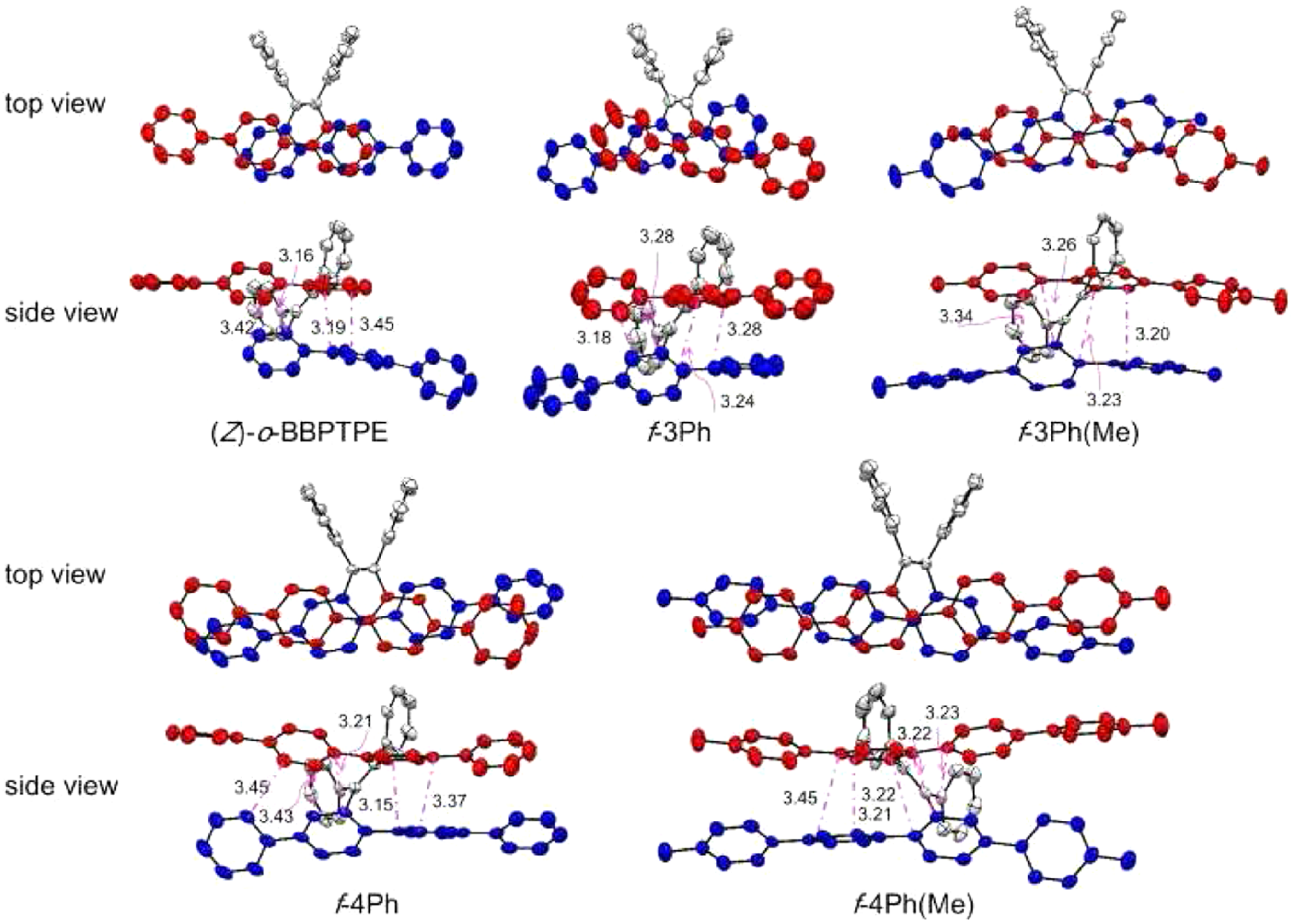

Figure 1. Crystal structures of folded fluorophores with indicated distances (Å) between π-stacked phenyl rings. Hydrogen atoms are omitted for clarity.

energy transfer and the balance of structural rigidity and flexibility are demonstrated to be responsible for both merits, that is, large Stokes shifts and high fluorescence efficiency.

The folded fluorophores were readily synthesized in moderate yields by McMurry coupling of oligo-*p*-phenylenes carrying a benzoyl group in the presence of $TiCl_4$ and zinc dust (Scheme 1). Whereas most McMurry couplings were non-stereospecific, the present reaction proceeded stereoselectively, affording products with a *cis*-conformation after forming an alkenyl group from two carbonyl groups. The possible mechanism was described in our previous work.[11] These folded fluorophores show distinctive doublet peaks at ∼ 6.0 ppm, assigned to the protons on the π-stacked phenyl rings, which are notably upfield-shifted compared to those of common aromatic protons, due to the shielding effect from another π-stacked phenyl ring.[11b,12] Examples of NMR spectra of *f*-3Ph, *f*-3Ph(Me), *f*-4Ph, and *f*-4Ph(Me) are displayed in Figure S1 in Supporting Information.

Single crystals of *f*-3Ph, *f*-3Ph(Me), *f*-4Ph, *f*-4Ph(Me), and (*Z*)-*o*-BBPTPE[11b] grown from THF/methanol or dichloromethane/hexane mixtures were analyzed by X-ray diffraction crystallography. Detailed parameters for the geometries of the crystal structures are given in Figures S2−S6. As displayed in Figure 1, the crystal structures validate a folded *cis*-conformation, where two oligo-*p*-phenylene chains, linked with an alkenyl bridge, are located closely in a roughly parallel manner. The shortest distances between slightly slipped, face-to-face phenyl rings are 3.16−3.46 Å, which are shorter than the typical distance for a π−π stacking interaction (3.5 Å), indicative of efficient intramolecular through-space conjugation[13] in these folded fluorophores. However, a longer oligo-*p*-phenylene chain does not mean a stronger π−π stacking interaction, as the longer oligo-*p*-phenylene chain becomes more twisted at both ends, making it difficult to form a regular π−π stacking between phenyl rings. This finding is consistent with the packing manner of linear oligo-*p*-phenylenes in the crystalline state.[14]

These folded fluorophores show absorption peaks at 275−308 nm in THF, which gradually move to the long-wavelength region with the increase of chain length (Figure 2). For instance, the absorption peak of *f*-3Ph is located at 275 nm, while that of *f*-5Ph shifts to 302 nm, equal to a red shift of 27 nm. The substitution of methyl groups on oligo-*p*-phenylene chains further pushes the absorption spectra to longer wavelengths. The absorption peaks of these folded fluorophores are consistent with the absorption of linear oligo-*p*-phenylenes, such as *p*-terphenyl (3Ph, 281 nm) and *p*-quaterphenyl (4Ph, 299 nm) (Figure S8, Table S1), demonstrating that the peaks are associated with the absorption of oligo-*p*-phenylene chains rather than the alkenyl-bridged entire molecular backbone.

Contrary to the chain-length sensitive absorption property, the photoluminescence (PL) peaks of the folded fluorophores in solutions are much more stable. Their PL maxima vary slightly in the range of 489−498 nm, which are very close to that of the archetypal folded fluorophore (*Z*)-*o*-BPTPE (493 nm)[11b] but extremely longer than those of linear oligo-*p*-phenylenes, such as

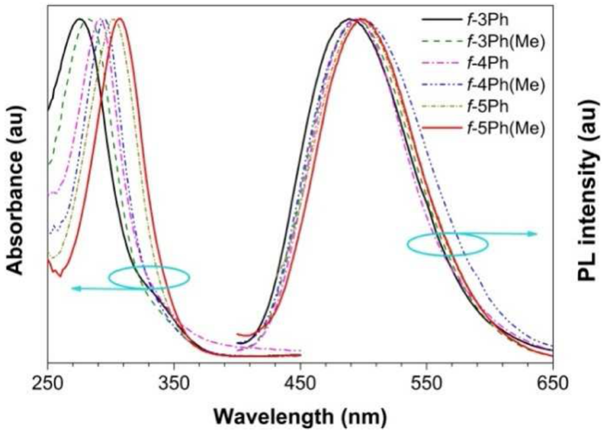

Figure 2. Normalized absorption and photoluminescence spectra of the folded fluorophores in THF solution (10^{-5} M).

3Ph (340 nm) and 4Ph (368 nm). This implies that the emissions originate from the central folded part (alkenyl-linked two biphenyl fragments) rather than from the entire fluorophores or the oligo-*p*-phenylene moieties. Hence, an interesting photophysical process occurs where the oligo-*p*-phenylene chains actually function as antennas, which harvest and transfer photonic energy to the central alkenyl-linked part for light emission. These fluorophores show only slight PL variations in nonpolar and high-polar solvents (Figure S9), showing the absence of an ICT effect.

These folded fluorophores show good PL emissions in THF, with high absolute fluorescence quantum yields (Φ_F) of 30−38% (Table 1). Their fluorescence lifetimes in THF are 6.5−8.6 ns (Table S2, Figure S10), which fall within the fluorescence region, revealing that the PL emissions originate from the radiative decay of the singlet excited state. The efficient PL emissions in THF of these folded fluorophores are really interesting because most tetraarylethenes are almost nonfluorescent in solutions with much shorter fluorescence lifetimes because the severe intramolecular rotation of aromatic rings nonradiatively deactivates the excited state.[15] The folded conformation should have greatly improved the molecular rigidity, and the rotational or torsional motions of the oligo-*p*-phenylene chains are suppressed significantly. Therefore, the nonradiative decay of the excited state is blocked, enabling molecules to fluoresce strongly in solution.

These folded fluorophores give enhanced emissions in the aggregated state (Figure S11). For example, the PL emission of *f*-4Ph(Me) intensifies with the increase of water fraction in THF/water mixtures (Figure 3). Since the hydrophobic *f*-4Ph(Me) is insoluble in water, aggregates of *f*-4Ph(Me) are formed in the aqueous environment. The PL enhancement occurs along with the aggregate formation, demonstrating the aggregation-enhanced emission (AEE) attribute. *f*-4Ph(Me) in the solid state is highly emissive, and its Φ_F increases to 58% in solid film, being nearly 2-fold higher than that in THF (30%), which further verifies its AEE feature. This is attributed to the two unstacked phenyl rings attached on the alkenyl group, which are free to rotate in solution and nonradiatively deplete part of the excited state energy. In aggregates, the rotation of the unstacked phenyl rings is restricted by the spatial constraint, and the nonradiative excited state decay is further depressed, rendering fluorophores even more emissive.

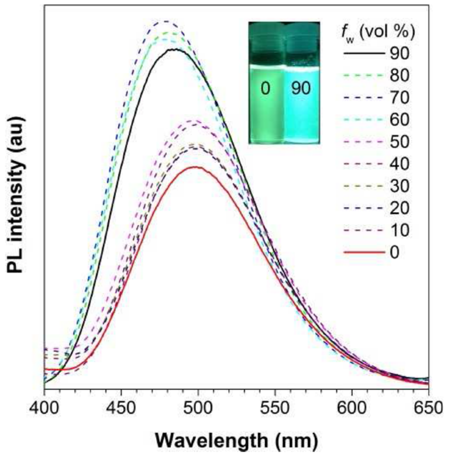

Figure 3. Photoluminescence spectra of *f*-4Ph(Me) in THF−water mixtures with different water fractions (f_w), excited at 330 nm. Inset: Photos of *f*-4Ph(Me) in THF−water mixtures (f_w = 0 and 90%), taken under the illumination of a UV lamp (365 nm).

The aggregate formation gives rise to blue-shifted PL spectra, and varied PL peaks are observed for the folded fluorophores in different aggregate states (Table 1, Figure S12). For example, the PL peak of *f*-4Ph(Me) is blue-shifted from THF solution (498 nm) to amorphous film (478 nm) and then to crystals (463 nm). This phenomenon should result from a more rigid molecular structure in the aggregated state, particularly in the crystalline state, in which the reorganization energy is lowered, leading to a decreased Stokes shift and, thus, blue-shifted emission.[16]

Notably, these folded fluorophores exhibit very large Stokes shifts in THF. As indicated in Figure 2, the differences between the absorption and emission peaks are in the range of 190−214 nm, which are rarely observed for pure hydrocarbon fluorophores. For instance, the Stokes shifts of linear oligo-*p*-

Table 1. Photophysical Properties of Folded Fluorophores

	λ_{abs} (nm)	λ_{em} (nm)			$\Delta(\lambda_{em}-\lambda_{abs})$ (nm)	Φ_F[c] (%)		
compound	soln[a]	soln[a]	film[b]	crystal	soln[a]	soln[a]	film[b]	$\langle\tau\rangle$[d] (ns)
(*Z*)-*o*-BBPTPE	280	492	472	454	212	32	61	7.0
f-3Ph	275	489	471	464	214	30	35	6.5
f-3Ph(Me)	282	492	470	451	210	32	37	8.0
f-4Ph	291	494	478	463	203	38	57	7.9
f-4Ph(Me)	295	498	478	463	203	30	58	8.6
f-5Ph	302	496	471		194	32	52	8.2
f-5Ph(Me)	308	498	470		190	30	67	8.5

[a] In THF solution (10^{-5} M). [b] Film drop-casted on a quartz plate. [c] Absolute fluorescence quantum yield measured by an integrating sphere. [d] Fluorescence lifetime determined in THF solution at room temperature in air.

phenylenes in the literature are <90 nm,[13] and those of 3Ph and 4Ph measured by us are merely 59 and 69 nm, respectively. Since the structural rigidity is improved in the aggregated state, the reorganization energy is decreased as discussed above, which diminishes the Stokes shifts (Table 1). Therefore, it becomes clear that, in THF, after the energy transfer to the central alkenyl-linked fragment, the rotational motion of the unstacked phenyl rings on alkenyl group consumes part of the energy, that is, enhanced reorganization energy, which red shifts the PL emissions, and leads to large Stokes shifts. Therefore, the freely rotatable unstacked phenyl rings should be crucial to the large Stokes shifts of these folded fluorophores. This is also evidenced by the much smaller Stokes shift (113 nm) of a folded terphenyl dimer without freely rotatable phenyl rings.[17] Hence, a balance between the rigidity from the π-stacked oligo-*p*-phenylenes and the flexibility from the unstacked phenyl rings accounts for the high fluorescence efficiency and large Stokes shift of these folded fluorophores.

In conclusion, a series of intriguing folded fluorophores composed of a pair of π-stacked oligo-*p*-phenylenes tethered with an alkenyl group have been readily synthesized and characterized. They showed good fluorescence in solutions and further enhanced fluorescence in aggregates (AEE). Meanwhile, remarkably large Stokes shifts of up to 214 nm were obtained. These interesting photophysical properties were realized by the energy transfer from absorptive oligo-*p*-phenylene chains to the central alkenyl-linked two biphenyl fragments and the balance between structural rigidity and flexibility of the fluorophores. The present folded fluorophores are excellent models for the study of hydrocarbon fluorophores with both high fluorescence efficiency and large Stokes shifts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03152.

> Synthesis information, single-crystal structures of *f*-3Ph, *f*-3Ph(Me), *f*-4Ph, and *f*-4Ph(Me), PL spectra of folded fluorophores in different states and different solvents, absorption and PL spectra of 3Ph and 4Ph, fluorescence decay curves, X-ray crystallography information, and parts of photophysical data (PDF)
>
> X-ray data of (*Z*)-*o*-BBPTPE (CIF)
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> X-ray data of *f*-3Ph(Me) (CIF)
>
> X-ray data of *f*-4Ph(Me) (CIF)
>
> X-ray data of *f*-3Ph (CIF)
>
> X-ray data of *f*-4Ph (CIF)

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Notes

The authors declare no competing financial interest.

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