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Towards Tetraradicaloid: The Effect of Fusion Mode on Radical Character and Chemical Reactivity

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Supporting Information Placeholder

ABSTRACT: Open-shell singlet diradicaloids display unique electronic, non-linear optical and magnetic activity and could become novel molecular materials for organic electronics, photonics and spintronics. However, design and synthesis of diradicaloids with a significant polyradical character is a challenging task for chemists. In this article, we report our efforts toward tetraradicaloid system. A series of potential tetraradicaloids by fusion of two *p*-quinodimethane (*p*-QDM) units with naphthalene or benzene rings in different modes were synthesized. Their model compounds containing one *p*-QDM moiety were also prepared and compared. Their ground-state structures, physical properties and chemical reactivity were systematically investigated by various experimental methods such as steady-state and transient absorption, two-photon absorption, X-ray crystallographic analysis, electron spin resonance, superconducting quantum interference device and electrochemistry, assisted by density functional theory calculations. It was found that their diradical and tetraradical characters show a clear dependence on the fusion mode. Upon the introducing of more five-membered rings, the diradical characters greatly decrease. This difference can be explained by the pro-aromaticity/anti-aromaticity of the molecules as well as the intramolecular charge transfer. Our comprehensive studies provide a guideline for the design and synthesis of stable open-shell singlet polycyclic hydrocarbons with significant polyradical characters.

I. INTRODUCTION

π -Conjugated polycyclic hydrocarbons (PHs) with open-shell singlet diradical ground state have recently attracted tremendous interest due to their unique electronic, optical and magnetic properties and potential applications in organic electronics, non-linear optics, spintronics, and energy storage devices.¹ According to broken symmetry density functional theory (DFT) calculations, any molecule with a non-zero diradical character in the ground state can be classified as a diradicaloid (diradical-like molecule). So far, various relatively stable PH-based open-shell singlet diradicaloids have been synthesized, for example, bisphenalenyls,² zethrenes,³ indenofluorenes,⁴ anthenes,⁵ and quinoidal rylene.⁶ Fundamental studies on the structure-diradical character-physical property relationships have revealed that

both the aromaticity and the steric strain played important roles in determining the ground-state electronic structure and physical property. The next natural target is to access stable open-shell singlet tetraradicaloids or even polyradicaloids, which may open the opportunities to investigate multiple spin interactions and molecular magnetism. However, this is a very challenging task for chemists because molecules with significant tetraradical character or polyradical character are supposed to be extremely reactive. In addition, the multiple radical character is also dependent on the interactions between individual spins, that is, too strong or too weak bonding interaction between the spins may result in too low or too high multiple radical character, respectively. Therefore, one must carefully tune the structures to reach a balance.

Figure 1. Resonance structures of the studied diradicaloid and tetraradicaloid systems with different fusion modes.

Tobe's group recently synthesized a potential tetraradicaloid hydrocarbon, the cyclic tetracyclopenta[defjkl,pqr,vwx]tetraphenylene (TCPTP). However, all experimental evidences imply that TCPTP is better described as a singlet diradicaloid with a moderate diradical character ($\gamma_0 = 0.258$) and a small tetraradical character ($\gamma_1 = 0.085$, calculated by LC-UBLYP/6-311+G(d,p) method based on the crystallographic structure).⁷ Our particular interest here is to synthesize and study the properties of a series of linear tetraradicaloids. Since our group previously reported several derivatives of the pro-aromatic heptazethrene (HZ) with moderate diradical characters (Figure 1a),^{3d,e,g} we first attempted to synthesize the fused heptazethrene dimer HZD (Figure 1b) which could exhibit both diradical and tetraradical characters. This sounds reasonable because from the closed-shell form to the diradical form and to the tetraradical form, one additional aromatic sextet ring (the hexagon highlighted in blue color) is gained, which can serve as the driving force to be open-shell diradical/tetraradical (Figure 1b). However, our results show that the target compounds, even after appropriate kinetic and thermodynamic stabilization, are so reactive and cannot be isolated and characterized. To obtain more stable

tetraradicaloids, we hypothesized that this can be done by introduction of two cyclopenta- rings to the molecular backbone because it was reported that many cyclopenta-fused polycyclic aromatic hydrocarbons (PAHs) are highly stable.⁸ We proposed two different fusion modes: in one case, the two outmost phenalenyl units in HZD are replaced by two indenyl moieties, resulting in a bis-fluoreno-pyrene structure FP (Figure 1c); in the other case, the central pyrene moiety in the HZD is replaced by an anti-aromatic *s*-indacene unit, leading to a bis-phenaleno-indenofluorene structure PIF (Figure 1d). Depending on whether it is a six-membered ring or a five-membered ring linkage between the *para*-quinodimethane (*p*-QDM) and the aromatic benzene or naphthalene units, the HZD, FP and PIF can be classified as 6-6-6-6, 5-6-6-5, and 6-5-5-6 fusion mode, respectively. For comparison, the derivatives of the linearly fused indenofluorene dimer IFD with a 5-5-5-5 fusion mode was also synthesized (Figure 1e).⁹ It is interesting to see that the ground state reactivity showed a strong dependence on the molecular fusion mode. For better understanding of the difference between fusion modes, three types of model compounds were prepared too, the heptazethrene HZ with a 6-6

Scheme 1. Synthesis of heptazethrene dimers **HZD-M** and **HZD-F**. *Reagents and conditions:* (a) $\text{Pd}(\text{PPh}_3)_4$, 2 M K_2CO_3 , toluene/ethanol, 105 °C, 12 h; (b) (i) ArMgBr , Ar = mesityl or pentafluorophenyl, dry THF, r.t., 12h, (ii) $\text{BF}_3 \cdot \text{OEt}_2$, dry DCM, r.t., 5 min; (c) DDQ, dry toluene, r.t.; (d) work up in air.

fusion mode (Figure 1a), the phenalenofluorene **PF** with a 6-5 fusion mode (Figure 1f) and the indenofluorene **IF** with a 5-5 fusion mode (Figure 1g). Their ground states and physical properties were systematically investigated by various experimental methods such as steady-state and transient absorption (TA), two-photon absorption (TPA), X-ray crystallographic analysis, electron spin resonance (ESR), superconducting quantum interference device (SQUID) and electrochemistry, assisted by DFT calculations.

II. RESULTS AND DISCUSSION

1. 6-6-6-6 system (HZD)

The fused heptazethrene dimers were synthesized *via* an intramolecular Friedel-Crafts alkylation followed by oxidative dehydrogenation strategy (Scheme 1). The building block **1** was first obtained by Suzuki coupling between 2,5-dibromobenzene-1,4-dicarboxaldehyde and (2-(hexyloxy)naphthalen-1-yl)boronic acid (see the Supporting Information (SI)). Suzuki coupling between **1** with (2,5-bis(hexyloxy)-1,4-phenylene)diboronic acid (**2**) gave the key intermediate tetraol **3**. The alkoxy chain was introduced to improve the solubility and also prevent the formation of five-membered ring containing isomers in the coming cyclization step. Treatment of **3** with mesitylmagnesium bromide or pentafluorophenylmagnesium bromide afforded the corresponding tetraol compounds, which were subjected to $\text{BF}_3 \cdot \text{OEt}_2$ mediated Friedel-Crafts alkylation reaction to give

the tetrahydro- precursors **4a/b**. The dehydrogenation of precursor **4a/b** was conducted by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in dry toluene at room temperature. However, this gave a quite reactive species (**HZD-M** and **HZD-F**) which could transform into the dioxo- compounds **HZD-M-ONE** and **HZD-F-ONE** (dark green solid) in one hour. Workup and purification of the reaction mixture in air afforded compounds **HZD-M-ONE** and **HZD-F-ONE**, respectively. The structures of **HZD-M-ONE/HZD-F-ONE** were unambiguously identified by NMR, high-resolution mass spectrometry (see SI), and X-ray crystallographic analysis.

X-ray crystallographic structure of **HZD-M-ONE** clearly disclosed a nearly planar molecular backbone, with the ketone groups formed at the *peri*- positions of the terminal naphthalene rings (Figure 2a).¹⁰ Bond length analysis of the backbone revealed a new PAH structure containing ten benzenoid rings, fused by two α,β -unsaturated ketone moieties (C1-C2: 1.344 Å; C2-C3: 1.450 Å; C3-O: 1.236 Å) (Figure 2b).

Broken symmetry DFT calculations (UCAM-B3LYP/6-31G(d,p)) were conducted to study the ground-state electronic structure and to understand the high reactivity of **HZD**. The singly occupied molecular orbital (SOMO) profiles of the α and β spins showed an obvious disjoint feature, indicating a large diradical character (Figure S1 in SI). Indeed, a large diradical character (y_0

Figure 2. (a) X-ray crystallographic structure of **HZD-M-ONE**; (b) selected bond lengths of the backbone of **HZD-M-ONE**; (c) calculated (UCAM-B3LYP) bond lengths, NICS(1)zz values and spin density distribution of the singlet diradical of parent **HZD**. (d) one-photon and two-photon absorption spectra of **HZD-M-ONE**. TPA spectra are plotted at $\lambda_{\text{ex}}/2$.

$=0.713$) was calculated, but the tetraradical character ($y_1 = 0.009$) turned out to be very small (Table 1). A small singlet-triplet energy gap ($\Delta E_{\text{S-T}} = -3.0$ kcal/mol) was predicted. The large diradical character explains the very high chemical reactivity of **HZD-M** and **HZD-F**, although they are stabilized by bulky mesityl groups (in **HZD-M**) or electron-deficient pentafluorophenyl groups (in **HZD-F**). The calculated bond lengths and NICS(1)zz values of the ground-state singlet diradical indicate large aromatic character for the rings A-C and E-F, implying a large contribution of the diradical form to the ground-state structure. On the other hand, the ring D has non-aromatic character (Figure 2c). The spin densities are evenly distributed throughout the whole π -conjugated backbone, and high spin density can be found at the *peri*-positions of the terminal naphthalene units (Figure 2c), which can explain why oxygen addition preferred to take place at these sites to generate the dioxo-products. The other reactive sites are kinetically blocked to a certain extent. We also attempted to conduct ESR measurements on the *in situ* generated **HZD-M** in a sealed ESR tube under nitrogen atmosphere. However, due to the high reactivity of this compound, it cannot be directly determined during the dehydrogenation reaction. An intense single-line ESR signal ($g_e = 2.00280$) was observed after adding the DDQ in 10 minutes (Figure S8 in SI). The variable temperature (VT) ESR measurements on the solid sample after removing the solvent under nitrogen showed that the ESR intensity (I) increased with decreasing temperature (T), with I being approximately proportional to $1/T$ (Figure S8 in SI), indicating that the major magnetically active species in the mixture is a mono-radical

intermediate rather than the diradical, which may be due to the high reactivity and the short lifetime of **HZD-M**. Experiments by using *in situ* generated **HZD-F** gave similar results.

Table 1. Calculated (UCAM-B3LYP) diradical character (y_0), tetraradical character (y_1) and singlet-triplet energy gap ($\Delta E_{\text{S-T}}$) for the parent systems.

Fusion mode	Comp	y_0	y_1	$\Delta E_{\text{S-T}}$ (kcal/mol)
6-6-6-6	HZD	0.713	0.009	-3.0
5-6-6-5	FP	0.635	0.003	-2.3
6-5-5-6	PIF	0.351	0.031	-4.2
5-5-5-5	IFD	0.038	0.005	-8.4
6-6	HZ	0.17	-	-8.1
6-5	PF	0.05	-	-9.1
5-5	IF	0.00	-	-13.2

The two dioxo- products **HZD-M-ONE**/**HZD-F-ONE** exhibit deep green color in both solid and solution phases. Their one-photon absorption spectra (OPA) in dichloromethane (DCM) are shown in Figure 2d and Figure S12 in SI and the data are summarized in Table 2. Compound **HZD-M-ONE** solution displays a well resolved spectrum with the absorption maximum at 667 nm ($\epsilon = 6580 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 1d and Table 2), which can be correlated to the HOMO→LUMO transition

Table 2. Photophysical and electrochemical data of the tetraradicaloids and model compounds.

Compd	λ_{abs} (nm)	ϵ_{max} (M ⁻¹ cm ⁻¹)	τ (ps)	$\sigma_{\text{max}}^{(2)}$ (GM)	$E_{1/2}^{\text{ox}}$ (V)	$E_{1/2}^{\text{red}}$ (V)	HOMO (eV)	LUMO (eV)	E_{g}^{EC} (eV)	$E_{\text{g}}^{\text{opt}}$ (eV)
HZD-M-ONE	450	11050	20 (τ_1)	1300 ^a	0.14	-1.67	-4.86	-3.23	1.63	1.75
	667	6580	2900 (τ_2)		0.72	-2.27				
	612	3380								
HZD-F-ONE	446	76220	2450	1400 ^a	0.55	-1.39	-5.3	-3.53	1.77	1.83
	643	52790				-1.95				
	591	28210								
FP-M	836	50750	25	1500 ^b	-0.26	-1.45	-4.41	-3.47	0.94	1.10
	960	6510			-0.05	-1.65				
	1005	9860			0.39	-1.84				
	1096	1550			0.67	-2.37				
PIF-M-ONE	355	56060	7.2	770 ^a	0.49	-1.41	-5.09	-3.54	1.57	1.85
	620	41260			0.95	-1.59				
PIF-F-ONE	357	51870	2.2	970 ^a	0.92	-1.00	-5.65	-3.87	1.78	1.83
	625	36530				-1.19				
						-1.99				
IFD-CF₃	367	53320	0.7 (τ_1)	800 ^c	0.49	-1.01	-5.25	-3.88	1.37	1.39
	662	23680	3.7 (τ_2)		0.74	-1.23				
	722	41420								
HZ-M	327	36590	55 (τ_1)	730 ^d	-0.27	-2.03	-4.47	-2.87	1.60	1.91
	613	70030	5500 (τ_2)		0.17	-2.36				
HZ-F	326	25220	80 (τ_1)	900 ^d	0.07	-1.67	-4.8	-3.23	1.57	1.90
	610	42180	5100 (τ_2)		0.47	-2.09				
PF-M	436	12440	7.2	400 ^a	-0.07	-1.87	-4.65	-3.03	1.62	1.56
	627	6760			0.62	-2.37				
PF-F	436	12440	7.2	410 ^a	0.25	-1.43	-4.98	-3.49	1.49	1.43
	627	6760			0.77	-1.97				
IF-M	515	42640	0.7 (τ_1)	--	0.71	-1.56	-5.41	-3.32	2.09	2.21
			14 (τ_2)			-2.07				
IF-CF₃	541	11530	0.6	--	0.89	-1.14	-5.64	-3.75	1.89	2.16
						-1.48				

λ_{abs} : absorption maximum. ϵ_{max} : molar extinction coefficient at the absorption maximum. τ is singlet excited-state lifetime obtained from TA in toluene. $\sigma_{\text{max}}^{(2)}$ is the maximum TPA cross section at the wavelength of: ^a1300 nm, ^b1700 nm, ^c1500 nm, ^d1200 nm measured in DCM. $E_{1/2}^{\text{ox}}$ and $E_{1/2}^{\text{red}}$ are half-wave potentials of the oxidative and reductive waves, respectively, with potentials vs Fc/Fc⁺ couple. HOMO and LUMO energy levels were calculated according to equations: HOMO = - (4.8 + $E_{\text{ox}}^{\text{onset}}$) and LUMO = - (4.8 + $E_{\text{red}}^{\text{onset}}$), where $E_{\text{ox}}^{\text{onset}}$ and $E_{\text{red}}^{\text{onset}}$ are the onset potentials of the first oxidative and reductive redox wave, respectively. E_{g}^{EC} : electrochemical energy gap derived from LUMO-HOMO. $E_{\text{g}}^{\text{opt}}$: optical energy gap derived from the lowest energy absorption onset in the absorption spectra.

(λ_{abs} = 688 nm, oscillator strength f = 0.7071) based on time-dependent (TD) DFT calculations (B3LYP/6-31G*) (see SI). Compound **HZD-F-ONE** with a different substituent group at the bay region shows a similar absorption spectrum to **HZD-M-ONE** (Figure S12 in SI). The excited-state dynamics of compounds **HZD-M-ONE**/**HZD-F-ONE** were investigated by femtosecond transient absorption (TA) measurements (Figure S9 in SI). The two compounds exhibit similar TA spectra with two ground-state bleaching (GSB) signals around 645 nm and 714 nm as well as a weak excited-state absorption (ESA) band in 450-630 nm. The singlet excited-state lifetimes (τ) of **HZD-M-ONE** and **HZD-F-ONE** were determined to be 2.9 ns and 2.5 ns, respectively. These singlet excited-state lifetimes are similar to those of typical fused PAHs. Due to the largely

extended π -conjugation, they are expected to exhibit remarkable hyperpolarizability. Therefore, two-photon absorption (TPA) measurements were conducted for these two compounds by Z-scan method in the wavelength range from 1200 to 1400 nm, where one-photo absorption (OPA) contribution is negligible (Figure 1d and Figure S10 in SI). Compound **HZD-M-ONE** exhibited a remarkable TPA cross-section maximum ($\sigma_{\text{max}}^{(2)}$) value of 1300 GM at 1300 nm, which is slightly smaller than that of compound **HZD-F-ONE** ($\sigma_{\text{max}}^{(2)}$ = 1400 GM at 1300 nm) (Figure S10 in SI). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were conducted to study the electrochemical properties of compounds **HZD-M-ONE**/**HZD-F-ONE** (Figure S11 in SI and Table 2). Compound **HZD-M-ONE** showed two

reversible oxidation waves at $E_{1/2}^{\text{ox}} = 0.14, 0.72$ V and two reversible reduction waves at $E_{1/2}^{\text{red}} = -1.67, -2.27$ V (vs. Fc/Fc^+ , Fc = ferrocene), while **HZD-F-ONE** showed one quasi-reversible oxidation waves at $E_{1/2}^{\text{ox}} = 0.55$ V and two reversible reduction waves at $E_{1/2}^{\text{red}} = -1.39$ and -1.95 V. The electrochemical energy gaps were calculated as 1.63 and 1.77 eV for **HZD-M-ONE** and **HZD-F-ONE**, respectively, which are consistent with their optical energy band gaps (Table 2).

2. 6-5-5-6 (FP) and 5-6-6-5 (PIF) systems

To obtain more stable materials, two cyclopenta rings were introduced and the synthesis of derivatives of the 5-6-6-5 fused **PF** and the 6-5-5-6 fused **PIF** were attempted. Similarly, bulky mesityl (in **PF-M** and **PIF-M**) or electron-withdrawing pentafluorophenyl (in **PF-F** and **PIF-F**) substituents were attached to the most reactive sites. The synthetic route for these compounds is shown in Scheme 2. Suzuki coupling of 2,5-dibromobenzene-1,4-dicarboxaldehyde with phenylboronic acid gave the key building block **5** in good yield (see SI). The key intermediate tetraaldehyde **6** was obtained by

Suzuki coupling between **5** and the boronic acid **2**. Then, compound **6** was treated with mesitylmagnesium bromide/pentafluorophenylmagnesium bromide followed by an intramolecular Friedel-Crafts alkylation reaction to afford the tetrahydro- precursors **7a/7b**. Compound **FP-M** was finally obtained as dark green solid by oxidative dehydrogenation of **7a** with DDQ at 80 °C for half an hour. However, the pentafluorophenyl substituted compound **7b** could not be dehydrogenated by DDQ even under reflux in toluene. This may be due to the very strong electron-withdrawing nature of pentafluorophenyl group. The synthesis of **PIF-M/PIF-F** tetrahydro-precursors **10a/10b** followed a similar strategy to the synthesis of **7a/7b**, but starting from the tetra-aldehyde intermediate **9** (Scheme 2). Similar to the **HZD-M/HZD-F** compounds the dehydrogenation of **10a/10b** only gave the dioxo- product **PIF-M-ONE/PIF-F-ONE** instead of the target **PIF-M/PIF-F** compounds. The structures of **FP-M**, **PIF-M-ONE** and **PIF-F-ONE** were identified unambiguously by NMR spectroscopy, high-resolution mass spectrometry, and crystallographic analysis (*vide infra*, and SI).

Scheme 2. Synthesis of **FP-M/FP-F** and **PIF-M/PIF-F**. *Reagents and conditions:* (a) $\text{Pd}(\text{PPh}_3)_4$, 2 M K_2CO_3 , toluene/ethanol, 105 °C; (b) (i) ArMgBr , Ar = mesityl or pentafluorophenyl, dry THF, r.t., 12h; (ii) $\text{BF}_3 \cdot \text{OEt}_2$, dry DCM, r.t., 5 min; (c) DDQ, dry toluene, 80 °C, 30 min; (d) DDQ, dry toluene, r.t.; (e) work up in air.

Compound **FP-M** only shows broadened ^1H NMR spectrum in solution even at low temperature (down to -100 °C Figure S13 in SI). **FP-M** in DCM exhibits a broad three-line ESR signal with $g_e = 2.0027$ (Figure 3a), and the signal intensity gradually decreases as temperature decreases,

indicating a singlet diradical ground state (Figure S14 in SI). The SQUID measurement was conducted to study the temperature dependent magnetic susceptibility behavior. The results show that its magnetic susceptibility increases as temperature increases after 100 K, which further implies a

singlet ground state for **FP-M** compound (Figure 3b). The singlet-triplet energy gap ($2J/k_B$, i.e., ΔE_{S-T}) was calculated to be -852.6 K (-1.69 kcal/mol) for **FP-M** by a careful fitting of the data using the Bleaney-Bowers equation (Figure 3b).¹¹ To further understand the magnetic properties of **PIF-M**, the *in situ* ESR test was also conducted. However, similar to **HZD-M**, only monoradical species were detected during the test. More specifically, the VT ESR measurements on the solid sample after removing the solvent under nitrogen showed that the ESR intensity (I) increased as temperature (T) decreased, with I being approximately proportional to $1/T$ (Figure S8 in SI), indicating that the formation of the mono-radical intermediates presumably due to extremely high reactivity of the diradical species.

Figure 3. (a) ESR spectrum of **FP-M** in DCM solution measured at r.t.; (b) χT -T plot for the solid **FP-M**. The measured data were plotted as open circles, and the fitting curve was drawn using Bleaney-Bowers equation with $g_e = 2.00$.

Single crystals suitable for crystallographic analysis were obtained for **FP-M**¹² and **PIF-M-ONE**¹³ by solvent diffusion methods and their structures are shown in Figure 4. **FP-M** shows a slightly twisted structure due to the steric congestion at the cove region (Figure 4a). Bond length analysis reveals that the length of the C1-C2 bond (1.400 Å) is significantly longer than the typical olefins (1.33-1.34 Å) but is much shorter than a typical C (sp²)-C (sp²) single bond (~1.45 Å), indicating a large contribution of the diradical form to the

ground state electronic structure (Figure 4b). DFT calculations (UCAM-B3LYP/6-31G(d,p)) indicate that the parent **FP** has an open-shell singlet ground state, with a moderate diradical character ($y_0 = 0.635$) and a very small tetraradical character ($y_1 = 0.003$) (Table 1). The singlet triplet energy gap was calculated to be -2.3 kcal/mol, which is close to the experimental data of **FP-M**. The calculated bond lengths are similar to the X-ray crystallographic data. Bond length analysis and the calculated NICS(1)zz values indicated a typical aromatic character for the rings A-C and E. On the other hand, cyclopenta ring D has a weak anti-aromatic character (Figure 4c). The spin densities are evenly distributed throughout the whole π -conjugated backbone (Figure 4c) and the calculated SOMO profiles of the α and β spins of **FP** (Figure S2a in SI) showed a typical disjoint feature.

PIF-M-ONE exhibits a slightly twisted structure (Figure 4d) and bond length analysis reveals an extended indenofluorene structure fused with two α,β -unsaturated ketone units (C1-C2: 1.392 Å; C2-C3: 1.401 Å; C3-O: 1.237 Å) (Figure 4e). It is worth noting that the oxygen was added at different position on the phenalenyl units compare to **HZD-M-ONE**. DFT calculations (UCAM-B3LYP/6-31G(d,p)) suggest that **PIF** also has an open-shell singlet ground state, with a moderate diradical character ($y_0 = 0.351$) and a small tetraradical character ($y_1 = 0.031$) (Table 1). The singlet-triplet energy gap was calculated to be -4.2 kcal/mol. Bond length and NICS(1)zz analysis of the ground-state singlet diradical of **PIF** indicate large aromatic character for rings E and F, weak aromatic character for rings A, C, D, and anti-aromatic character for ring B (Figure 4f). The α and β spins show similar disjoint feature and the spin densities are also evenly distributed throughout the whole π -conjugated backbone (Figure 4f and Figure S2b in SI). Although **PIF** has a smaller diradical character and larger singlet-triplet energy gap than **FP**, it seems that the two terminal phenalenyl units are more prone to be attacked by oxygen and become more reactive. However, it is not clear why the reaction takes place at the site C3 rather than C1 as both have similar spin density.

The green-color solution of **FP-M** in DCM shows a strong absorption at 836 nm ($\epsilon = 50750 \text{ M}^{-1} \text{ cm}^{-1}$) and several weak absorption bands with peaks at 960, 1005 and 1096 nm in the lower energy region (Figure 5a and Table 2). Similar to many other singlet diradicaloids, the lowest-energy absorption band likely originates from the presence of a low-lying singlet excited state dominated by a doubly excited electronic configuration (H,H $\rightarrow$ L,L).¹⁴ It is also worth noting that the dilute solution of **FP-M** is almost transparent due to its intense and sharp near IR-absorption and weak absorption in the visible region, indicating that **FP-M** molecule could have potential technological application as near-IR dye.

Figure 4. (a) X-ray crystallographic structure of **FP-M**; (b) selected bond lengths of the backbone of **FP-M**; (c) calculated (UCAM-B3LYP) bond lengths, NICS(1)zz values and spin density distribution of the singlet diradical of parent **FP**; (d) X-ray crystallographic structure of **PIF-M-ONE**; (e) selected bond lengths of the backbone of **PIF-M-ONE**; (f) calculated (UCAM-B3LYP) bond lengths, NICS(1)zz values and spin density distribution of the singlet diradical form of the parent **PIF**.

The di-oxo- product **PIF-M-ONE** shows a very different spectrum with a broad band at 620 nm (Figure 5b). In accordance with this spectrum, TD DFT calculations (B3LYP/6-31G*) predicted a strong HOMO→LUMO transition at 639.2 nm ($f = 1.0033$) (Figure S7b in SI). **PIF-F-ONE** shows almost the same OPA spectrum as **PIF-M-ONE** (Figure S12b in SI). The TA spectrum of **FP-M** exhibits a strong GSB signal around 820 nm and two ESA bands in the 450–720 and 880–950 nm (Figure S9 in SI). The singlet excited-state lifetime was estimated to be 25 ps. TA spectra of **PIF-M-ONE** is similar to **PIF-F-ONE**. Both of them have a GSB signal around 630 nm as well as two weak ESA bands in 450–525 nm and 670–850 nm (Figure S9 in SI). Their singlet excited-state lifetimes were determined to be 7.2 and 2.2 ps, respectively. Similarly, TPA measurements were conducted and **FP-M** exhibited a remarkable cross-section maximum value $\sigma_{\max}^{(2)}$ of 1500 GM at 1700 nm, which is much larger than that for the closed-shell compounds **PIF-M-ONE** and **PIF-F-ONE** ($\sigma_{\max}^{(2)} = 770$ and 970 GM, respectively). This enhanced nonlinear optical property of **FP-M** can be explained by its moderate open-shell diradical character.¹⁵

Compound **FP-M** displays well-resolved eight-stage amphoteric redox behavior with four oxidation waves at $E_{1/2}^{\text{ox}} = -0.26, -0.05, 0.39, 0.67$ V and four reduction waves at $E_{1/2}^{\text{red}} = -1.45, -1.65, -1.84, -2.37$ V (vs Fc/Fc) in the CV/DPV measurements (Figure S11 in SI). Electrochemical energy gap of **FP-M** was determined as 0.94 eV, which is consistent with those obtained from

Figure 5. One-photon and two-photon absorption spectra of (a) **FP-M**, (b) **PIF-M-ONE**. TPA spectra are plotted at $\lambda_{\text{ex}}/2$.

the optical onset (Table 2). Compound **PIF-M-ONE** displayed two quasi-reversible oxidation waves at $E_{1/2}^{\text{ox}} = 0.49, 0.95$ V and two reversible reduction waves at $E_{1/2}^{\text{red}} = -1.41, -1.59$ V

(vs Fc/Fc^+). On the other hand, **PIF-F-ONE** showed only one quasi-reversible oxidation waves at $E_{1/2}^{\text{ox}} = 0.92$ V and three reversible reduction waves at $E_{1/2}^{\text{red}} = -1.00, -1.19, -1.99$ V due to the electron-withdrawing effect of the pentafluorophenyl substituents (Figure S11 in SI). The electrochemical energy gaps were calculated as 1.57 and 1.78 eV for **PIF-M-ONE** and **PIF-F-ONE**, respectively, which are consistent with their optical energy band gaps (Table 2).

3. 5-5-5-5 (IFD) system

To further understand the effect of the fusion mode on diradical/tetradiradical characters and chemical reactivity, the 5-5-5-5 fused indenofluorene dimers were also synthesized (Scheme 3). The tetraaldehyde intermediate **11** was obtained *via* the Suzuki coupling between **5** and **8** in 90% yield. Treatment of **11** with aryl magnesium bromide followed by an intramolecular Friedel-Crafts alkylation reaction gave the tetrahydro-precursors **12a/b/c** with different substituents. First, the oxidative dehydrogenation of the bulky mesityl precursor **12b** with DDQ was conducted. A dark-green solid product was obtained and the mass was matched with the target product (see SI). However, due to the very poor solubility of the product in common organic solvents, it is difficult to do further characterization. Unfortunately, the pentafluorophenyl substituted precursor **12c** could not be dehydrogenated by DDQ even under reflux in toluene. Finally, we found that 3,5-bis(trifluoromethyl)phenyl substituted precursor **12a** could be easily dehydrogenated and the product **IFD-CF₃** has a good solubility in common solvents. The structure of **IFD-CF₃** was unambiguously identified by NMR, high-resolution mass spectrometry (see SI) and X-ray crystallographic analysis.

Single crystal of **IFD-CF₃** was obtained *via* solvent diffusion method and its structure is shown in Figure 6a.¹⁶ **IFD-CF₃** shows a fully planar backbone. The bond length analysis on the molecular backbone reveals that the bond lengths for *a* (1.392 Å) and *c* (1.365 Å) exhibit significant double-bond character, whereas the bond *b* (1.431 Å) has single-bond character (Figure 6b). The large bond alternation indicates a significant contribution of the close-shell resonance form to the ground state. DFT calculations (UCAM-B3LYP/6-31G(d,p)) predicted that the parent **IFD** has a very small diradical character ($y_0 = 0.038$) and a large singlet-triplet energy gap ($\Delta E_{\text{S-T}} = -8.4$ kcal/mol). In accordance with this, **IFD-CF₃** showed sharp NMR signals in solution and there was no detectable ESR signal for both solution and solid. Therefore, **IFD-CF₃** is better to be described as a closed-shell compound. NICS(1)zz calculations suggest that **IFD** can be regarded as an anti-aromatic hydrocarbon in which two anti-aromatic indenofluorene units are annealed together *via* a weak aromatic benzene ring *a* (Figure 6b).

The electronic absorption spectrum of **IFD-CF₃** in DCM showed an intense absorption band at 722 nm ($\epsilon = 41420 \text{ M}^{-1} \text{ cm}^{-1}$) with a long tail extending beyond 1000 nm (Figure 6c and Table 2). This spectral feature is similar to that for the anti-aromatic indeno[2,1-*b*]fluorene itself containing $4n$ monocyclic conjugated π electrons. TD DFT calculations (B3LYP/6-31G*) on the closed-shell form predicted a strong HOMO→LUMO transition at 802.6 nm ($f = 1.0936$), which is attributable to the absorption at 722 nm, and a weak forbidden HOMO-1→LUMO transition at 890.8 nm ($f = 0.0238$), which can be correlated to the long tail. The TA spectrum of **IFD-CF₃** exhibited a strong GSB signal around 725 nm and two weak ESA bands in

Scheme 3. Synthesis of **IFD-CF₃**, **IFD-M** and **IFD-F**. *Reagents and conditions:* (a) $\text{Pd}(\text{PPh}_3)_4$, 2 M K_2CO_3 , toluene/ethanol, 105 °C, 12 h; (b) (i) ArMgBr , $\text{Ar} =$ mesityl, pentafluorophenyl or 3,5-bis(trifluoromethyl)phenyl, dry THF, r.t., 12h, (ii) $\text{BF}_3 \cdot \text{OEt}_2$, dry DCM, rt, 5 min; (c) DDQ, dry toluene, reflux, 12 h.

450–580 and 760–850 nm (Figure S9 in SI). The singlet excited-state lifetime was estimated to be 3.7 ps. The TPA measurement was also conducted to investigate its nonlinear optical properties (Figure 6c and Figure S10 in SI). **IFD-CF₃** exhibited a cross-section $\sigma_{\text{max}}^{(2)}$ of 800 GM at 1500 nm, which

is smaller than **FP-M**, presumably due to its large anti-aromatic character. Electrochemical measurements were conducted for **IFD-CF₃** (Table 2 and Figure S11 in SI). Two oxidations at $E_{1/2}^{\text{ox}} = 0.49, 0.74$ V and two reductions at $E_{\text{red}}^{1/2} = -1.01, -1.23$ V (vs Fc/Fc^+) were observed. Accordingly, the

electrochemical energy gap was estimated to 1.37 eV, which is close to the optical energy gap.

Figure 6. (a) X-ray crystallographic structure of **IFD-CF₃**; (b) selected bond lengths of the backbone of **IFD-CF₃**; insert are the calculated (UCAM-B3LYP) NICS(1)zz values of the parent IFD; (c) one-photon and two-photon absorption spectra of **IFD-CF₃**. TPA spectra are plotted at $\lambda_{ex}/2$.

4. 6-6/6-5/5-5 model compounds and discussion

As can be seen above, the fusion model has significant influence on the ground-state electronic structures and chemical reactivity. To better understand the origins of this difference, three kinds of model compounds were synthesized (Figure 1 and Scheme 4). The 6-6 fused **HZ**, the 6-5 fused **PF** and the 5-5 fused **IF** can be regarded as the model compounds for **HZD**, **FP** and **IFD**, respectively. The dialdehyde intermediates **13/14** were first prepared by Suzuki coupling using the above mentioned building blocks (see SI). Similar reaction sequence including addition of aryl Grignard reagents, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ mediated intramolecular Friedel-Crafts alkylation and DDQ mediated oxidative dehydrogenation gave the desired model compounds in good yields. Compounds **IF-M** and **IF-CF₃** were synthesized according to Haley's method.^{4c}

Scheme 4. Synthesis of model compounds **HZ-M/HZ-F**, **PF-M/PF-F** and **IF-M/IF-CF₃**. *Reagents and conditions:* (a) R-MgBr, R = mesityl, pentafluorophenyl or 3,5-bis(trifluoromethyl)phenyl, dry THF, r.t., 12h; (b) $\text{BF}_3 \cdot \text{OEt}_2$, dry DCM, r.t., 5 min; (c) DDQ, dry toluene, r.t. for **HZ-M/HZ-F**, **PF-M/PF-F**; (d) SnCl_2 , dry toluene, 80 °C.

To better understand the difference between the three types of monomers, compounds **HZ-M**, **PF-M** and **IF-M** with the same mesityl substituents were compared. The characterizations and physical properties of the other compounds are shown in SI. All the three compounds exhibit clear and sharp NMR signal, indicating their closed-shell character in the ground state. Single crystals suitable for crystallographic analysis were obtained for **HZ-M**¹⁷ and **PF-M**¹⁸ via solvent diffusion method and the X-ray crystallographic structure of **IF-M** was previously reported^{4a} and directly used here for comparison. Both **HZ-M** and **IF-M** exhibit a planar structure while the unsymmetric **PF-M** shows a slightly twisted structure (Figure 7a-c). Bond length analyses reveal that the central *p*-QDM unit in three compounds shows large bond length alternation (Figure 7d-f), indicating their quinoidal characters. DFT calculations (UCAM-B3LYP/6-31G(d,p)) predicted that **HZ** has a small diradical character ($y_0 = 0.17$). On the other hand, **PF** and **IF** have a negligible diradical character ($y_0 = 0.05$) and a zero diradical character, respectively (Table 1). The calculated NICS(1)zz values indicate that from **HZ** through **PF** to **IF**, the central benzene ring becomes more anti-aromatic (Figure 7d-f). Fundamentally, **HZ** can be regarded as a pro-aromatic system, while **IF** is an anti-aromatic system, and the **PF** is in between. Looking into

the resonance forms of **PF** (Figure 1f), besides the closed-shell quinoidal form and open-shell diradical form, a dipolar zwitterionic form could also contribute significantly to the ground state structure, which may explain its smaller diradical character in comparison to **HZ**. Such difference after incorporation of cyclopenta rings dramatically affects their ground states and physical properties.

Figure 7. X-ray crystallographic structures (a-c) and selected bond lengths of the backbones (d-f) of **HZ-M**, **PF-M** and **IF-M** (c). Insert are the calculated (UCAM-B3LYP) NICS(1)zz values of the parent **HZ**, **PF** and **IF**.

The electronic absorption spectra of the three compounds in DCM are compared (Figure 8a). The 6-6 fused **HZ-M** displays a well resolved spectrum with an intense *p*-band at 613 nm ($\epsilon = 70030 \text{ M}^{-1} \text{ cm}^{-1}$), which can be correlated to HOMO→LUMO transition ($\lambda_{\text{abs}} = 655.9 \text{ nm}$, $f = 0.7036$) based on TD DFT calculations (B3LYP/6-31G*). The 5-5 fused compound **IF-M** shows a typical absorption spectrum of anti-aromatic compounds with an intense band at 515 nm ($\epsilon = 42640 \text{ M}^{-1} \text{ cm}^{-1}$) and a weak absorption tail extending to 700 nm. TD DFT calculations predicted an intense HOMO→LUMO transition at 518.7 nm ($f = 0.5126$), while the HOMO-1→LUMO transition (606.2 nm, $f = 0.0$) is forbidden. The similarity between the absorption spectrum of **IF-M** (also **IF-CF3**, see Figure S12 in SI) and that of **IFD-CF3** indicates both have an anti-aromatic character. The unsymmetric 6-5 fused **PF-M** exhibits a very different

absorption spectrum, with a moderately intense band at 436 nm ($\epsilon = 12440 \text{ M}^{-1} \text{ cm}^{-1}$) and a broad band extending into the near-IR region. The long-wavelength broad absorption could originate from the intramolecular charge transfer which is very common in many unsymmetric dipolar molecular systems. In consistence with experimental results, TD DFT calculations predicted a broad absorption at 658 nm (HOMO→LUMO transition, $f = 0.3826$) and two close transitions at 463.1 nm (HOMO-1→LUMO transition, $f = 0.1319$) and 435.6 nm (HOMO→LUMO+1 transition, $f = 0.1999$) (Figure S7 in SI). Compounds **HZ-M**, **PF-M** and **IF-M** also displayed distinctly different TA spectra in DCM (Figure 8b-d). The TA spectrum of **HZ-M** exhibited a GSB signal around 620 nm as well as a weak ESA band in 450-550 nm and around 820 nm (Figure 8b). The singlet excited-state lifetime was determined to be 5500 ps. Such long excited-state lifetime could be explained by its small diradical character. **PF-M** displayed an intensive GSB signal around 630 nm and two intense ESA signals at 450-600 and 680-800 nm (Figure 8c). The singlet excited-state lifetimes was estimated to be 7.2 ps. The 5-5 fused system **IF-M** shows a GSB signal at 450-540 nm with a strong ESA signal at 550-800 nm. Due to its anti-aromatic nature, it shows a very short excited-state lifetime (14 ps), similar to the alkyne-substituted indenofluorene.¹⁹ Therefore, the singlet excited-state lifetimes dramatically decreased and the intensity of ESA band increases going from the pro-aromatic **HZ-M** to the intermediate dipolar **PF-M** and the anti-aromatic **IF-M**. The discussion in principle can go further to explain the observed phenomenon for the potential tetraradicaloid systems **HZD**, **FP**, **PIF** and **IFD**. Similar to **HZ**, the fused dimer **HZD** can be also regarded as a pro-aromatic system. Due to the extended conjugation, the diradical character largely increases, leading to a highly reactive species. After incorporation of two cyclopenta rings, besides the closed-shell quinoidal and open-shell diradical forms, a dipolar ionic form also contributes significantly to the ground state, which results in a decrease of the diradical character as observed in **FP** and **PIF**. Reasonable stability can be achieved if the reactive sites with high spin density are appropriately protected (as seen in **FP-M**). When four cyclopenta rings are incorporated, the obtained **IFD** becomes a typical anti-aromatic compound with very small diradical character, and stable materials can be obtained after kinetic blocking the reactive sites. TPA measurements disclosed that **HZ-M** showed larger $\sigma_{\text{max}}^{(2)}$ value (730 GM at 1200 nm) than **PF-M** (400 GM at 1300 nm) (Table 2 and Figure S10 in SI), presumably due to its larger diradical character. Since our Z-scan set-up can only measure the TPA spectrum from 1200 nm to 2400 nm, the TPA spectrum of **IF-M** around 500 nm region could not be obtained.

Figure 8. (a) One-photon absorption spectra of **HZ-M**, **PF-M** and **IF-M** in DCM; and the transient absorption spectra of (a) **HZ-M**, (b) **PF-M** and (c) **IF-M** recorded in toluene. Inserts are the decay profiles.

CV and DPV measurements were conducted to study the electrochemical properties of these three model compounds **HZ-M**/**PF-M**/**IF-M** (Figure S11 in SI and Table 2). Compound **HZ-M** gave two reversible oxidation waves at $E_{1/2}^{\text{ox}} = -0.27, 0.17 \text{ V}$ and two reversible reduction waves at $E_{1/2}^{\text{red}} = -2.03, -2.36 \text{ V}$ (vs Fc/Fc^+), while compound **IF-M** showed one oxidation waves at $E_{1/2}^{\text{ox}} = 0.71 \text{ V}$ and two quasi-reversible reduction waves at $E_{1/2}^{\text{red}} = -1.56$ and -2.07 V . The unsymmetric compound **PF-M** display two oxidation waves at $E_{1/2}^{\text{ox}} = -0.07, 0.62 \text{ V}$ and two reduction waves at $-1.87, -2.37 \text{ V}$. The electrochemical energy gaps were determined as 1.60, 2.09 and 1.62 eV for **HZ-M**, **IF-M** and **PF-M**, respectively, which are consistent with their optical energy band gaps (Table 2).

Although our original intention is to synthesize stable compounds with significant tetradical character, all the four systems we studied should be better described as diradicaloids because the tetradical characters are substantially small. It seems that it is not an easy task to achieve a real tetradical character. Nakano *et al.* recently calculated the polyradical characters in the linear H-H-H-H tetradicaloid system and suggested that the diradical character (γ_0) and tetradical character (γ_1) are determined by the interactions between the four spins and moderate coupling would result in a significant tetradical character while unbalanced interactions would lead to a decreased tetradical character.²⁰ Applied to our case, we believe that small tetradical characters are caused by unbalanced, too strong radical-radical couplings between the

four spins. Therefore, this is a key factor we must consider seriously in our future design.

III. CONCLUSIONS

In summary, we have synthesized a series of linear potential tetradicaloids by fusion of two *p*-QDM units with aromatic benzene or naphthalene rings in different modes. Their model compounds were also prepared and compared. It turned out that the fusion mode have dramatic effect on the ground-state electronic structures, diradical character and tetradical characters, and chemical reactivity. The HZ dimer **HZD** has a large diradical character and is highly reactive and gave dioxo-product upon contact with air. Upon introducing two cyclopenta rings in **FP** and **PIF**, the diradical character greatly decreases. The indenofluorene dimer **IFD** with four cyclopenta rings has a very small diradical character and behaves as a closed-shell compound. These differences could be explained by the pro-aromatic/anti-aromatic character of the molecules and the intramolecular charge transfer effect based on the model compound studies. Due to unbalanced radical-radical interactions, these compounds exhibited small tetradical character and are better described as diradicaloids with tunable diradical character. Our comprehensive studies provide insight into the design and synthesis of stable open-shell singlet polyradicaloids in the future.

ASSOCIATED CONTENT

Supporting Information. Synthetic procedures and characterization data of all other new compounds; details for all physical characterizations and theoretical calculations; additional spectroscopic and X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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10. Crystallographic data for **HZD-M-ONE**: $C_{106}H_{110}O_6$, $M_w = 1480.04$; monoclinic; space group P-1; $a = 15.7254(8) \text{ \AA}$, $b = 16.3000(8) \text{ \AA}$, $c = 19.7644(10) \text{ \AA}$, $\alpha = 88.0843(9)^\circ$, $\beta = 73.1877(9)^\circ$, $\gamma = 70.5165(9)^\circ$; $V = 4560.7(4) \text{ \AA}^3$; $Z = 2$; $\rho_{\text{calcd}} = 1.252 \text{ Mg/m}^3$; $R1 = 0.0640$ ($I > 2\sigma(I)$), $wR2 = 0.1934$ (all data). CCDC No.: 1436511.
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12. Crystallographic structures for **FP-M**: $C_{86}H_{84}O_2$, $M_w = 1148.65$; monoclinic; space group P 2(1)/c; $a = 9.2447(4) \text{ \AA}$, $b = 27.6365(10) \text{ \AA}$, $c = 14.8907(5) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 98.658(3)^\circ$, $\gamma = 90^\circ$; $V = 3761.1(2) \text{ \AA}^3$; $Z = 4$; $\rho_{\text{calcd}} = 1.178 \text{ Mg/m}^3$; $R1 = 0.0530$ ($I > 2\sigma(I)$), $wR2 = 0.1368$ (all data). CCDC No.: 1434045.
13. Crystallographic structures for **PIF-M-ONE**: $C_{102}H_{110}O_6$, $M_w = 1430.83$; triclinic; space group P-1; $a = 10.9480(4) \text{ \AA}$, $b = 12.0802(4) \text{ \AA}$, $c = 16.2323(6) \text{ \AA}$, $\alpha = 69.553(2)^\circ$, $\beta = 76.264(2)^\circ$, $\gamma = 79.814(2)^\circ$; $V = 1943.58(12) \text{ \AA}^3$; $Z = 1$; $\rho_{\text{calcd}} = 1.222 \text{ Mg/m}^3$; $R1 = 0.0570$ ($I > 2\sigma(I)$), $wR2 = 0.1578$ (all data). CCDC No.: 1436512.
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16. Crystallographic structures for **IFD-CF3**: $C_{78}H_{50}F_{24}O_2$, $M_w = 1475.22$; monoclinic; space group C 2/c; $a = 32.7089(12) \text{ \AA}$, $b = 14.2715(5) \text{ \AA}$, $c = 15.6260(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 104.233(2)^\circ$, $\gamma = 90^\circ$; $V = 7070.4(5) (12) \text{ \AA}^3$; $Z = 8$; $\rho_{\text{calcd}} = 1.386 \text{ Mg/m}^3$; $R1 = 0.1243$ ($I > 2\sigma(I)$), $wR2 = 0.3981$ (all data). CCDC No.: 1434047.
17. Crystallographic structures for **HZ-M**: $C_{58}H_{60}O_2$, $M_w = 789.06$; monoclinic; space group C2/c; $a = 26.3642(16) \text{ \AA}$, $b = 16.1386(9) \text{ \AA}$, $c = 23.420(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 119.4610(18)^\circ$, $\gamma = 90^\circ$; $V = 8676.1(11) \text{ \AA}^3$; $Z = 8$; $\rho_{\text{calcd}} = 1.208 \text{ Mg/m}^3$; $R1 = 0.0513$ ($I > 2\sigma(I)$), $wR2 = 0.1481$ (all data). CCDC No.: 1436513.
18. Crystallographic structures for **PF-M**: $C_{48}H_{46}O$, $M_w = 638.90$; monoclinic; space group P 2(1)/n; $a = 14.9865(5) \text{ \AA}$, $b = 7.9786(3) \text{ \AA}$, $c = 34.6321(12) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 101.364(2)^\circ$, $\gamma = 90^\circ$; $V = 4059.8(2) \text{ \AA}^3$; $Z = 4$; $\rho_{\text{calcd}} = 1.196 \text{ Mg/m}^3$; $R1 = 0.0497$ ($I > 2\sigma(I)$), $wR2 = 0.1335$ (all data). CCDC No.: 1434048.
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21. Crystallographic structures for **HZ-F**: $C_{52}H_{38}F_{10}O_2$, $M_w = 884.86$; triclinic; space group P-1; $a = 7.7536(3) \text{ \AA}$, $b = 8.4647(4) \text{ \AA}$, $c = 16.2224(8) \text{ \AA}$, $\alpha = 83.656(2)^\circ$, $\beta = 80.330(2)^\circ$, $\gamma = 65.6020(10)^\circ$; $V = 954.85(8) \text{ \AA}^3$; $Z = 2$; $\rho_{\text{calcd}} = 1.539 \text{ Mg/m}^3$; $R1 = 0.0457$ ($I > 2\sigma(I)$), $wR2 = 0.1282$ (all data). CCDC No.: 1434046.

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