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Excitonically Coupled Cyclic BF ₂ Arrays of Calix[8]- and Calix[16]phyrin as Near-IR-Chromophores

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Dedicated to Professor Atsuhiro Osuka on the occasion of his retirement from Kyoto University

Abstract: Two giant calix[n]phyrin derivatives namely calix-[8]- (4) and calix[16]phyrin (5), involving two and four BF 2 units, respectively, were prepared through the condensation of window as compared to single chromophore systems and the bis-naphthobipyrrolylmethene-BF2 complex (3) with pentafluorobenzaldehyde. Calix[n]phyrins 4 and 5 display extremely high extinction coefficients (3.67 and 4.82 10⁵m⁻¹cm⁻¹, respectively) in the near-IR region, which was taken as initial evidence for strong excitonic coupling within these cyclic multi-chromophoric systems. Detailed insights into dipyrromethene), which has been explored for a wide variety the effect of excitonic coupling dynamics on the electronic structure and photophysical properties of the macrocycles came from fluorescencetime-correlated single-photon counting (TCSPC) and transient absorption (TA) measurements. Support for these experimental findings came from theoretical studies. Theory and experiment confirmed that the coupling between the excitons depends on the specifics of the calix-[n]phyrin structure, not just its size.

Introduction

Chromophore arrays displaying strong excitonic interactions are of current interest for the design of artificial photosynthetic antenna mimics and for creating constructs

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capable of solar energy harvesting.^[1] Strong excitonic coupling between chromophores helps widen the absorption generally improves the light-capturing efficiency.^[2] Organic molecules displaying very high absorbance over a broad spectral range including in the near IR region and exhibiting strong exciton coupling are particularly attractive in this regard.^[3] One chromophore of interest is BODIPY (boronof applications, including light-harvesting, fluorescent probe development, and photodynamic therapy (PDT).^[4] Covalently linked cyclic arrays of dipyrromethene BF 2 units are expected to be more effective for light-harvesting than simple monomeric BODIPYs, particularly if they possess good excitonic coupling. One way to bring multiple BODIPY units into proximity and potentially enforce excitonic coupling would be to exploit oligopyrrolic frameworks, such as socalled expanded porphyrins and calixphyrins.^[5] However, cyclic BODIPY arrays made up of such macrocycles are relatively unexplored.^[6, 7] The inherent stability expected for such putative covalently linked polychromophores over, e.g., self-assembled cyclic or cage-like BF 2 arrays, makes them further appealing for light-harvesting applications.^[8] We recently reported a bowl-shaped trimeric cyclic BODIPY system derived from a hybrid expanded porphyrin that can act as an effective photosynthetic antenna mimic and supramolecular host for Li⁺@C₆₀^[9] Furuta, Kim, and Fukatsu have shown that tri- and tetrameric BODIPY arrays derived from N-confused calix[n]phyrin derivatives display unique photophysical and useful lasing properties.[7a] Nabeshima and coworkers prepared several macrocyclic BODIPY arrays incorporating 1,4- and 1,3-phenylene moieties and explored them as hosts for cationic guests.^[10] However, the photophysical properties of these reported macrocyclic BODIPY systems are limited, in that they mostly absorb and emit light in the visible range of the electronic spectrum (typically below 600 nm). Furthermore, except in one instance, [9] most of these

Furthermore, except in one instance, ^[9] most of these reported BODIPY arrays were not explored in the context of light-harvesting. There is thus a need for BODIPY arrays with absorption and emission features over the NIR spectral region if the full potential of BODIPY-based approaches in generating artificial photosynthetic antenna mimics is to be realized. Appropriate BODIPY arrays can be prepared by linking BODIPY units in a linear or cyclic manner using strong excitonic coupling between BODIPY units. Understanding the determinants that lead to effective excitonic

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coupling is an essential aspect of this exercise. However, linearly-linked arrays often have structural flexibility and thus exhibit shorter lifetimes due to the presence of increased nonradiative deactivation channels compared to those in the corresponding monomer subunits^[11] Cyclic arrays can, at least in principle, exist in more rigid structures since each BODIPY unit is locked in place by neighboring units. To the extent it is achieved, such structural rigidity would be expected to reduce the rate of nonradiative relaxation. This, in turn, should lead to a prolongation of the excited state lifetimes of the system as a whole, which could prove advantageous in terms of creating light-harvesting systems.

With such considerations in mind, we have now prepared two giant cyclic BODIPY systems, namely calix[8]phyrin-1.0.1.0) (5). These macrocyclic arrays contain two and four BF₂ units, respectively. In contrast to earlier reported systems, these new poly-BODIPY arrays display intense NIR absorptions. As detailed further below, ¹H NMR spectroscopic analyses carried out in CD₂Cl₂ at room temperature provide support for the conclusion that both 4 and 5 are relatively rigid and exist in a single conformation on the NMR time scale. This conformational integrity is thought to enhance excitonic coupling between the individual chromophore subunits. Both macrocycles 4 and 5, as well as precursors 2 and 3 used to prepare them, have been characterized thoroughly by various spectroscopic methods, as well as single-crystal X-ray structural analyses. A combination of ground and excited state optical measurements and theoretical studies provide support for the presence of strong excitonic coupling in these cyclic BODIPY di- and tetramers. This coupling is thought to account for the intensity of the absorption features. However, there are notable differences between the two calix[n]phyrins of the present study. Specifically, the larger system (5), which possesses a three-

dimensional structure, exhibits panchromatic absorption

features and a longer excited-state lifetime than either dimer 4 or monomer 3. Thus, the present study serves to underscore how changes in structure can be used to modulate the photophysical properties of multichromophore arrays.^[12]

Results and Discussion

Synthesis and Characterization

The goal of the present study was to create large oligopyrrolic frameworks containing multiple BODIPY-like fluorogenic centers. To avoid possible complexities associated with post-synthetic functionalization, we elected to use the 0.bis-naphthobipyrrolylmethene-BF₂ complex 3 as the key precursor. A further incentive for this particular choice of s, building blocks was the thinking that the relatively large size of this chosen building block might limit the number of possible products formed during macrocyclization.^[13] In this context, we note the growing interest in using BODIPY-based precursors to construct novel expanded porphyrins^[6b,e,f, 14]

Previously, the Panda group reported a meso-free, tetra-balkylated version of 3 with impressive photophysical properties.^[15] This made 3 additionally attractive as a possible control compound. It was converted into products 4 and 5 as shown in Scheme 1. Briefly, condensation of 3 (2 mm in CH₂Cl₂) with pentafluorobenzaldehyde yielded macrocycle 4 and 5 in 5 % and 32 % isolated yield, respectively, after chromatographic purification (see Supporting Information for complete preparative details). Precursor 3, itself was prepared from unsubstituted naphthobipyrrole 1 in two straightforward steps. Specifically, the reaction of naphthobipyrrole 1 with mesitaldehyde in the presence of TFA (trifluoroacetic acid) as an acid catalyst yielded bis-naphthobipyrrolylmethene 2 in up to 53 % yield after chromatographic purification, followed by recrystallization. In contrast



Scheme 1Synthesis of the BF complexes of the calix[n]phyrins 4 and 5 considered in this study (n = 8 and 16, respectively).

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to what is typically seen in condensations involving bipyrroles of 4 revealed a gable-type structure along with the two sp ³ and aromatic aldehydes, including pentafluorobenzaldehyde, no rosarin formation was observed under the reaction conditions.^[16] Precursor 2 was then converted to its corresponding BODIPY complex 3 by treating with BF ₃·OEt₂ in the presence of triethylamine in accord with standard protocols.[15]

3 revealed near-planar structures (Supporting Information, Figures S25 and S26^[17] This planarity and the rigidity were considered likely to favor the formation of larger cyclic systems, as seen experimentally (see below).

Macrocycles 4 and 5 were initially characterized by MALDI-TOF mass spectrometry. These analyses revealed mass peaks of 1533.0320 and 3064.8640 amu, corresponding to molecular formulas of C $_{90}H_{52}B_2F_{14}N_8$ and C $_{180}H_{104}B_{14}F_{28}N_{16}$, respectively (Figures S23 and S24).

The ¹H NMR spectrum of 4 recorded in CD ₂Cl₂ at room temperature was characterized by the presence of an NH signal at 10.5 ppm integrating to a total of two hydrogen atoms as would be expected for compound 4. A resonance corresponding to the aromatic CH-protons was observed in the 8.2–7.0 ppm spectral range. In contrast, the signal for the unoxidized meso CH protons (integrating to two protons) was found to resonate at 6.87 ppm. The ¹¹B NMR spectrum was characterized by a broad signal at 2.6 ppm. In contrast, the ¹⁹F NMR spectrum of 4 recorded in CD ₂Cl₂ at room temperature revealed the presence of two fluorine signals corresponding to the BF 2 subunits at 138.1 and 141.5 ppm, respectively. The presence of these two signals is thought to reflect the asymmetry of the macrocycle in solution thus mirroring the gable-like structure seen in the solid state (Figure 1 a-c). Two signals corresponding to six hydrogens each were also observed for the two ortho CH groups of the mesityl substituents in the ¹H NMR spectrum. This is as expected for a conformationally rigid system with two formally distinct faces.

A single crystal X-ray diffraction analysis of crystals grown by the slow diffusion of hexanes into CHCl₃ solutions



Figure 1. Single-crystal X-ray structure of calix[8]phyrin 40Ha) Front view, b) side view and, c) p-p interactions in 4, meso-aryl substituents and H-atoms are omitted for clarity.

hybridized meso-like position bearing pentafluorophenyl substituents.^[17] Presumed p-p interactions between the naphthalene units of a neighboring molecule were inferred from the short separations (3.517), which presumably serve to stabilize the one-dimensional array seen in the solid state (Figure 1 a-c). However, no evidence of aggregation was Single crystal X-ray structural analyses of precursors 2 and observed when 4 was dissolved in dichloromethane (Figures S32–S35). The dihedral angle between the two planes defined by the individual bis-naphthobipyrrolylmethene unit was found to be 80.01 8. The centroid-to-centroid distance between the chromophoric units (defined by the C 29N4B planes, that is, the bis-naphthobipyrrolylmethene skeleton) was 7.898 (Table 1).

> Table 1:Selected conformational parameters for calix[n]phyrins 4 and 5 as inferred from X-ray structural data.

Entry	q [8] ^[a]	R [] ^[b]	R _{FF} [8] ^[c]
4	80.01	7.898	4.11
5	80.92 ⁰ 46.74 ^{e]}	11.429 ^ŋ 10.790 ^ŋ	9.122 ^{aj} 7.157 ^{ej}

[a] Dihedral angle between 20 AB planes. [b] Centroid-to-centroid distance between G₀N₄B planes. [c] Minimum distance between two F-atoms of different BF₂ units. [d] adjacent units. [e] co-facial units.

The ¹H NMR spectrum of calix[16]phyrin 5 recorded in CD₂Cl₂ at room temperature shows a set of NH-signals at 9.8 and 9.7 ppm that corresponds to a total of eight NH-protons as expected for 5. A singlet at 6.0 ppm accounts for the four meso-sp-CH protons. The ¹¹B NMR spectrum was characterized by the presence of a broad signal at 2.2 ppm. The ¹⁹F NMR spectrum also shows a broad signal at 140.3 ppm corresponding to the F-atom of the BF₂ subunits, rather than the split signal seen in the case of 4. Signals corresponding to the ortho, para, and meta CF fluorine atoms appeared at

142.7 (o), 143.2 (o), 153.4 (p) and 160.6 (m) ppm, respectively. On this basis, we conclude that system 5 is relatively symmetric in solution.

Further insights into the molecular structure of calix-[16]phyrin 5 came from single-crystal X-ray structural analyses of crystals grown through the slow diffusion of hexanes into a dichloroethane solution of 5.^[17] In the solid state, 5 exists as a three-dimensional box-like structure wherein four bis-naphthobipyrrolylmethene subunits are connected through four sp³-hybridized meso carbon atoms. The pentafluorophenyl groups are oriented towards the macrocyclic cavity. On the other hand, the four meso-mesityl groups point toward the outside of the cavity (Figure 2).

The four BF₂ units, like the pentafluorophenyl groups, point inwards, generating what is presumably a hydrophobic core. Evidence of the hydrophobic nature of the core came from the finding that complete exchange of the inner pyrrolic NH protons by deuterium could not be achieved even after contacting with D 2O for 20 days (Figure S17). The dihedral angle between the planes defined by two neighboring bisnaphthobipyrrolylmethene units (C $_{20}N_4B$) was found to be 80.928, whereas the angle between the tilted co-facial units

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Figure 2.Single-crystal X-ray structure of calix[16]phyrin 5. a) Front view and b) crystal packing pattern viewed along the c-axis.

was found to be 46.748. The centroid-to-centroid distance between the adjacent chromophoric units (defined by the $C_{29}N_4B$ units) was found to be 11.429, whereas the tilted cofacial units are separated by a relatively short distance (10.790). Thus, in comparison to the cyclic dimer 4, larger interchromophoric distances are observed for 5 in the solid state (Table 1).

Optical Properties UV/Vis/NIR Absorption and Emission Studies

The UV/Vis/NIR absorption and emission spectra of the acyclic monomer 3, cyclic BODIPY dimer 4, and cyclic BODIPY tetramer 5 recorded in toluene are shown in Figure 3. The monomer 3 shows an intense band at 728 nm with a very high molar extinction coefficient (e = 2.05 $10^5 m^1 cm^1$) with a presumed 0–1 vibronic band at 661 nm. In comparison to monomer 3, the dimer (calix[8]phyrin 4) shows two excitonically coupled bands at 696 nm (allowed) and 806 nm (forbidden), respectively. The separation between the excitonically split bands (110 nm) is greater than what was seen in the dimeric calixarene-like cyclic BODIPY system reported by the Brçring group.^[7b] The intensity of the



Wavelength / nm

Figure 3.UV/Vis/NIR absorption and emission spectra of compounds 3, 4, and 5 recorded in toluene at room temperature. Inset represents magnified forbidden transition band of 4.

absorption maxima (I $_{max}$) of 4 was found to be significantly enhanced (1.8-fold) relative to that of its constituent monomer 3. Although the lowest transition (806 nm) is forbidden the corresponding 0–1 vibronic transition is clearly observed at 735 nm (a feature confirmed as not being due to a monomer impurity). The 0–1 vibronic transition (1200 cm⁻¹) is comparable to the corresponding 0–1 vibronic transition of the monomer 3 (1400 cm⁻¹).

In contrast to the above, the absorption spectrum of calix[16]phyrin 5 is characterized by the presence of three excitonically coupled bands at 697 nm (allowed), 737 nm (allowed), and 776 nm (slightly allowed). The molar extinction coefficient for the formal tetramer 5 is larger than those for the monomer 3 (by 2.35-fold) and dimer 4 (by 1.31-fold), as calculated at the ${\sf I}_{\rm max}$ of the systems in question. In fact, the overall light absorption properties of tetramer 5 (as well as 4 to a lesser extent) are enhanced across the UV/Vis to NIR spectral region (250 to 800 nm) compared to the constituent monomer 3. For instance, at the wavelength of minimum light absorption (i.e., approx. 550 nm), the molar absorptivities of tetramer 5 proved nearly 9.7-fold greater than those of 3 (e = 7.8 vs.0.8 10^3 m⁻¹ cm⁻¹). The high molar absorptivities (e = approx. 0.08 to 4.80 10⁵ m¹ cm¹) seen for 5 over the 250-800 nm spectral region were found to be comparable or better than those of other known chromophores exhibiting panchromatic absorption.[18] We thus suggest that calix[16]phyrin 5 may have a role to play as an initial light capture chromophore.

The fluorescence spectrum of monomer 3 mirrors its absorption spectrum and is characterized by a maximum at 740 nm with a comparatively large quantum yield (f = 0.246; Figure 4 a). In contrast, the fluorescence spectrum of 4 was characterized by a maximum at 840 nm and a very low electronic state. In the case of tetramer 5, the fluorescence maximum is located at higher energy (I_{max} = 793 nm) relative to 4, in line with the energy levels of the lowest electronic transitions (forbidden states) formed through the excitonic coupling (Figure 4 c). Tetramer 5 exhibits a fluorescence quantum yield (f $_{\rm F}$ = 0.057) that is larger than that for dimer 4. Such a finding is consistent with the molecular structure of calix[16]phyrin 5 being such that the transition dipole moments of each constituent BODIPY unit are not perfectly aligned to cancel one another out. This stands in contrast to what is inferred in the case of the smaller system 4. The origin of these disparate effects is discussed further below.

Excitonic Coupling Calculations

An effort was made to understand the observed steadystate absorption features in terms of intramolecular exciton coupling effects. In the case of calix[n]phyrins 4 and 5, sp³ hybridized carbons serve to bridge the constituent BODIPY units. Conjugation effects are thus likely to be negligible. Rather, through-space exciton couplings between individual BODIPY monomers analogous to 3 are expected to play a critical role in terms of defining the excited states and the lowest electronic transitions. To a first approximation, the

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Figure 4. Experimental absorption spectra and calculated electronic transitions of a) 3, b) 4, and c) 5, in which the calculated transitions are redshifted (by 4000 cm¹) to allow useful comparisons with the experimental results and d) schematic diagrams of the energy levels of the exciton coupled states of 3 (left), 4 (middle), and 5 (right) showing the direction of the transition dipole moments for the constituent BODIPY units.

lowest electronic transition of monomer 3 is oriented along the long molecular axis. In the case of 4 and 5 these dipoles can orient to produce two and four exciton coupled states, respectively (Figure 4 d).An effort was thus made to underwere simulated by means of TD-DFT calculations carried out at the B3LYP/6-31G(d) level (Table S5). In dimer 4 the two BODIPY constituent units are connected such that their long molecular axes lie parallel to one another within an overall planar structure. As a result, two excitons coupled states are is below that of the monomer S_i state. The separation energy (1960 cm⁻¹) inferred from the experimental absorption spectrum is reproduced by the TD-DFT calculation (2430 cm⁻¹) and one (the lower state) is found to be forbidden while the other (the higher state) is allowed. In the case of the tetrameric BODIPY system 5, there are four exciton coupled transitions. One lies above and the other three transitions lie below the monomer S₁ state. The lowest electronic transition is forbidden; however, the remaining three are allowed (similar oscillator strengths). The two exciton coupled states (second and third transitions) are almost degenerate.

Secondly, the energies of the exciton coupled states and the associated coefficients of the transition dipole moments in in greater detail, fluorescence lifetime studies were carried each BODIPY unit were calculated. This was done using the matrix diagonalization method the details of which, including the equations and exciton coupling energy matrices, are included in the Supporting Information. For calix[8]phyrin 4, for which exciton coupling between only two units need to be considered, the separation energy between the exciton

coupled states was calculated to be 1900 cm⁻¹. This value, obtained without matrix diagonalization, is in accord with the experimental results (1960 cm¹). For tetramer 5, the relative energies of the four possible excitons coupled states were stand the possible couplings. Firstly, the electronic transitions calculated using the matrix diagonalization method and found to be 472, 23, 23, and 426 crhshifted from the monomer S state (Figure S37). It should be noted, however, that the calculated difference between the first and fourth exciton coupled states (900 cm¹) proved smaller than that derived by experiment (about 1460 cm¹). This stands in contrast to what formed in which the energy of one state is above and the other was seen in the case of 4. The lowest transition for 5 was also calculated to be strictly forbidden, which would lead to perfect quenching. However, as noted above, this tetrameric BODIPY system was found to display moderate fluorescence with a quantum yield of 0.057. The disparities between the experimental and calculated results for tetramer 5 lead us to suggest that the actual molecular structure differs from the optimized one such that full cancellation of the four transition dipole moments does not occur.

Fluorescence Lifetime Measurements

In order to probe the lowest electronic states of 3, 4, and 5 out in toluene employing time-correlated single-photon counting (TCSPC) measurements following photo-excitation at 450 nm (Figure 5). The fluorescence decay profiles were fitted with double-exponential functions convoluted with an instrumental response function (IRF) of 30 ps. Dynamics in the picosecond regime are presumed to reflect structural

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Figure 5. Fluorescence decay profiles of a) 3, b) 4, and c) 5 in toluene.

relaxation processes, while spectral changes occurring on the Transient Absorption Spectroscopy nanosecond time scale were thought to reflect the fluores-

cence lifetimes. On this basis, the fluorescence lifetimes for 3, The radiative/non-radiative rates, calculated using the experimentally determined fluorescence quantum yields and lifetimes, are listed in Table 2 (see below). The radiative rates, which represent the intrinsic emission, are smaller for 4 $(0.10 \ 10^7 \text{ s}^{-1})$ and 5 $(1.13 \ 10^7 \text{ s}^{-1})$ than for 3 $(6.78 \ 10^7 \text{ s}^{-1})$. This finding is ascribed to the forbidden nature of the lowest electronic transitions within the cyclic BODIPY dimer 4 and tetramer 5. On the other hand, the non-radiative rate of 4 is similar to that of monomer 3, while that of 5 is decreased. Such findings provide support for the inference that the new cyclic BODIPYs (4 and 5) preserve their structural rigidity in the photoexcited state.

Table 2: Selected photophysical properties of the BODIPY systems 3, 4, and 5.

Entry	L _{abs} [m]	l _{fl} [nm]	е	f _F ^[d]	t _F [ns] ^{a]}	k,	k _{nr}
			[10 ⁵ m ¹ cm ¹]			[10 ⁷ s ⁻¹] ^[b]	[10 ⁸ s ⁻¹] ^[c]
3	728 (max)	740	2.05 (max)	0.246	3.63	6.78	2.08
4	696 (max)	840	3.67 (max)	0.003	3.04	0.10	3.28
5	737 (max)	793	4.82 (max)	0.057	5.04	1.13	1.87

[a] t_F = fluorescence lifetime. [b]_r \Leftarrow radiative rate. [c] k = non-radiative rate where $1/t_{\rm F} = k_{\rm r} + k_{\rm nr}$ [d] Relative quantum yield was obtained using IR-14Q \neq f0.167) as the reference dye^[19]

The excited-state dynamics of 3, 4, and 5 were further 4. and 5 were found to be 3.63, 3.04, and 5.04 ns, respectively investigated by means of transient absorption (TA) measurements (Figure 6 and Figure S38). Marked bleaching of the ground state signals was observed near their absorption maxima. In contrast, relatively broad and weak excited state absorption signals were observed. Stimulated emission signals could also be detected readily at around 820 nm in the case of 3 but proved hard to detect in the case of 4 and 5, presumably because the radiative rates are very slow. In line with the fluorescence dynamics measured by TCSPCall compounds (3, 4, and 5) exhibit decay features within the approximate 100 ps decay window rather on the nanosecond lifetimes expected for an S state. Since the 100 ps events do not affect the S₁ state population, the slow structural relaxation process

seems to play a role in regulating the excited state dynamics. After and during such relaxation processes, fluorescence-based radiative relaxation and intersystem crossing compete. The control system 3 was found to give rise to more noticeable spectral changes than 4 and 5 in the circa 100 ps timescale. The differences in the signals in the spectral region corresponding to ground state bleaching region are readily attributed to changes in the excited-state absorption and stimulated emission signals reflecting structural changes in the excited state, rather than,



Figure 6. Transient absorption spectra of a) 3, b) 4, and c) 5 in toluene until 2 ns with 700 nm pump. Insets show the kinetics associated with the ground state bleaching region.

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assignment and the differences seen between the acyclic and Radiation Facility for assistance during the single crystal Xcyclic species are considered reasonable given the fact that monomer 3 is less rigid than 4 and 5, which are conformationally locked to a greater or lesser degree.

Conclusion

In conclusion, we have reported synthesis, structures, and The authors declare no conflict of interest. characterizations of two new cyclic BODIPY systems 4 and 5 containing two and four constituent BF 2 units, respectively. Both 4 and 5 are relatively stable under ambient laboratory conditions even though they comprise potentially oxidizable porphyrinogen-like frameworks. These cyclic BOIPY arrays absorb well in the NIR spectral region and are characterized by higher extinction coefficients at their absorption maxima (3.67 and 4.82 10⁵ m¹ cm⁻¹ for 4 and 5, respectively) than various previously reported BODIPY chromophore svstems.^[20] Detailed photophysical studies, including time-resolved fluorescence and transient absorption measurements. revealed excitonic coupling between the constituent chromophoric units in 4 and 5. While dimer 4 shows a slightly reduced excited-state lifetime and an extremely low radiative rate, tetramer 5 shows an increased lifetime and better radiative properties. These features are ascribed to the structural rigidity of this calix[16]phyrin and orientation that supports weakly allowed transitions, respectively. This BODIPY tetramer also exhibits absorption characteristics that could make it of interest as a panchromatic material. Theoretical calculations (TD-DFT) were found to reproduce well the experimental results. Likewise, matrix diagonalization analyses based on Kashas exciton coupling theory provided support for the proposed exciton coupling dynamics within 4 and 5. The present results highlight how appropriate structural design can lead to multi-chromophoric systems with attractive light-absorbing and excitonic coupling features. As such, it sets the stage for the preparation of more advanced artificial light-harvesting systems.

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for instance, singlet fission or energy transfer processes. This for Protein Science Shanghai and the Shanghai Synchrotron ray data collection. We thank Ms. Yanfei Niu and Prof. Xiaoli Zhao at East China Normal University for collecting the Xray data for compound 3.

Conflict of interest

Keywords:calix[n]phyrins cyclic BODIPY exciton coupling · NIR dyes ·porphyrinoids

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