Modulation of the Nonlinear Optical Properties of Dibenzo[*hi,st*]ovalene by Peripheral Substituents

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Abstract

Dibenzo[*hi,st*]ovalene (DBOV) is a nanographene molecule with quasi-zero dimensional electronic confinement, which displays relatively high oscillator strength, remarkable photostability and optical gain property. For these reasons, DBOV has been proposed as gain medium and active material for achieving strong exciton-photon coupling in microcavity. Here, we study the stimulated emission properties of three DBOV derivatives with different substitution patterns. We found that these molecules likely undergo ultrafast intermolecular charge transfer processes occurring within their π -aggregates, which ultimately leads to quenching of stimulated emission and increase of the amplified spontaneous emission threshold. These effects can be minimized by installing bulky substituents on the peripheries that prevent π - π stacking. We can thus selectively favor either the luminescence/gain properties or the charge transport features by engineering the side groups.

Keywords: nanographene; charge transfer; stimulated emission; amplified spontaneous emission; ultrafast spectroscopy

The geometric confinement of graphene into few nanometers has allowed to open a finite band-gap in its electronic structure, which rendered the resulting nanographenes highly promising for a range of optoelectronic applications.¹⁻³ Top-down approaches have been successfully used to fabricate nanographenes that are represented by *quasi*-1D graphene nanoribbons (GNRs),⁴ and *quasi*-0D graphene quantum dots (GQDs),⁵ although with certain degree of defects. On the other hand, bottom-up synthesis has provided atomically precise GNRs⁶⁻⁷ and molecular GQDs.^{6, 8-9} The latter approach has offered efficient control over energy gap and optical absorption/emission by tailoring the size and edge structures.^{6, 10-13} Such bottom-up synthesized nanographenes are thus highly promising for applications in the field of nanotechnology, optics, and optoelectronics.¹⁴⁻¹⁵

Toward photonic applications, nanographene molecules have attracted a growing research interest very recently, owing to their optical absorption and luminescence properties that depend strongly on the degree of nanoconfinement and edge configuration.¹⁶⁻²² A large variety of GNRs and molecular GQDs with armchair edges have been synthesized and characterized by various methods,^{6, 13} but there are still limited number of reports on nanographenes with zigzag edge although they generally exhibit intriguing properties, such as low energy gaps, biradical ground states character, and localized edge states.^{12, 16-17, 22-25} This is mainly due to the synthetic challenge in the incorporation of zigzag edges and their high environmental instability, which hampers their characterizations and utilization as functional materials.²⁶ To this end, we have recently proposed dibenzo[*hi,st*]ovalene (DBOV) as a new molecular GQD with both armchair and zigzag edges, which displays remarkable stability, low energy gap, high oscillator strength, and a photoluminescence quantum yield (PLQY) as high as 79%.²⁷ Moreover, DBOV exhibits optical gain properties, amplified spontaneous emission (ASE) with a relatively low excitation threshold for organic emitters ($60 \mu\text{J cm}^{-2}$),²⁷ and, interestingly, strong polaritonic emission at room temperature in microcavity.²⁸

In our previous spectroscopic investigation on DBOV,²⁷ we have noticed a relationship between the stability of the stimulated emission (SE) signal and intermolecular distance. Indeed, we have observed a dramatic and ultrafast (within 200 fs) quenching of SE when passing from solution (lifetime ≈ 300 ps) to solid films, whereas we were able to partially restore SE in diluted polymer matrix. We have tentatively attributed this effect to the formation of intermolecular polaronic-like species in solid film, whose absorption overlaps effectively with the SE band, in analogy with the photodynamic landscape depicted for conjugated polymers.²⁹⁻³¹ Although the aggregation behavior as well as the charge transport properties in supramolecular adducts of graphene molecules, in particular hexa-*peri*-hexabenzocoronene derivatives, has been studied extensively,³² to date there are no detailed reports on the possible impact that charge generation in nanographenes can have on their optical properties. Such information can be highly relevant for the applications of nanographenes as

emitters in light-emitting diodes and lasers, and as charge transport materials in solar cells and photodetectors.

Here, we report spectroscopic studies on DBOV derivatives with different substituents, providing evidence for strong competition between stimulated emission and charge generation in nanographenes. By systematically engineering the peripheral substituents, we found that the more substituted **DBOV-Mes-C12** exhibits a sensibly slower SE deactivation dynamic (> 1 ns)³³ and lower ASE threshold in polystyrene (PS) matrix ($60 \mu\text{J cm}^{-2}$) than the less functionalized **DBOV-Mes** ($180 \mu\text{J cm}^{-2}$) and **DBOV-Ph** (no ASE observed) (see Figure 1a for the structures). We attribute this effect to the higher tendency of the less functionalized DBOVs to form π -stacking aggregates with intermolecular charge transfer (CT) character, in which charges quench stimulated emission.

The structures of **DBOV-Mes-C12**, **DBOV-Mes**, and **DBOV-Ph** are displayed in Figure 1a and the synthesis was carried out through the method which we reported previously (see the SI).²⁷⁻²⁸ The peripheral substituents were varied to modify the propensity for aggregation: **DBOV-Mes-C12** carries two bulky mesityl groups and two dodecyl chains and **DBOV-Mes** possesses only two mesityl groups while the **DBOV-Ph** has two smaller phenyl groups. The absorption spectra of these three derivatives in toluene (Figure 1b) show similar spectral features: i. a relatively strong peak at 626 nm, 609 nm and 608 nm for **DBOV-Mes-C12**, **DBOV-Mes**, and **DBOV-Ph**, respectively, corresponding to the $0 \rightarrow 0'$ electronic transition; ii. two weaker vibronic replica at 563-576 nm ($0 \rightarrow 1'$) and 513-520 nm ($0 \rightarrow 2'$); iii. a broad absorption band peaked at 340-370 nm that can be attributed to a convolution of more energetic transitions (for the density functional theory calculations see S.I.).²⁷⁻²⁸

The lower $I_{0-0'}/I_{0-1'}$ ratio of **DBOV-Ph** (2) than that of **DBOV-Mes-C12** (2.8) and **DBOV-Mes** (2.7), and the appearance of a broad and red-shifted band for the less substituted molecules (**DBOV-Mes** and **DBOV-Ph**) (Figure 1b, inset), suggest the formation of stable π -stacked aggregates especially for the molecules lacking alkyl substitution.^{33-34 35} In addition, we embedded the three derivatives into a polystyrene (PS) matrix at 1 wt%, a weight ratio that was already optimized for observing PL and ASE action in **DBOV-Mes-C12**.²⁷ The optical absorption of the films (Figure 1c) shows regular fringes that can be attributed to interference phenomena (see Figure S4 for the reflection spectra), which in-fact hinder a detailed UV-VIS absorption characterization of the diluted blends in polymer matrix. On the other hand, the PLE spectra (Figure 1d and 1e for solutions in toluene and PS films) are a more sensitive probe for discriminating the different behavior of the three derivatives. In the toluene solutions, a larger FWHM is observed for **DBOV-Mes** (39 nm) and **DBOV-Ph** (36 nm) compared to that of **DBOV-Mes-C12** (24 nm), together with relatively higher PLE signal in the UV region (350-400 nm) when normalized at the PLE maxima. Furthermore, a decreased $I_{0-0'}/I_{0-1'}$ ratio is revealed for **DBOV-Mes** (1.2) and **DBOV-Ph** (1.3) in comparison with

DBOV-Mes-C12 (2). All these point toward a stronger tendency for the least substituted molecules to establish dipolar intermolecular interactions and form π -stacking aggregates. Although the narrower FWHM of the 0-0' PLE peaks in PS matrix (18 nm for the three molecules) indicates a larger intermolecular distance than in the 0.1 mg/mL solutions, the higher PLE signal in the 350-400 nm region for **DBOV-Mes** and especially for **DBOV-Ph** can be attributed to the partial retaining of aggregates also in the relatively diluted solid matrix. Although we observe some of the typical spectroscopic signatures of H-aggregation for these nanographenes, further experiments are currently underway to elucidate the exact nature of this phenomenon.

Figure 1. (a) Molecular sketches of the three DBOV derivatives. (b,c) UV-VIS absorption spectra of the three derivatives (b) in toluene solution (0.1 mg/ml) and (c) in PS matrix (DBOV:PS 1wt % ratio). (d,e) PLE spectra of the DBOV derivatives (d) in toluene solution (0.1 mg/ml) and (e) in PS matrix (DBOV:PS 1wt % ratio).

In **Figure 2** we present the differential transmission spectra and dynamics in toluene solution (0.1 mg/mL) and PS matrix. The transient spectra of the DBOV molecules (Figure 2 a,b,d,e,g,h,) display three main peaks, namely: i. a negative feature at around 500 nm that can be linked to photoinduced absorption (PA) from the first excited state (S_1) to higher lying states (S_n); ii. the main peak centered at 625 nm for **DBO1** and 610 nm for **DBOV-Mes** and **DBOV-Ph**, can be attributed to

the depletion of the ground state due to the $0 \rightarrow 0'$ transition (photobleaching PB); iii. a side positive peak at 560-570 nm corresponding to its vibronic replica ($0 \rightarrow 1'$); iv. a positive peak at 670-680 nm that can be associated to the stimulated emission signal (SE).²⁷ The spectra of the three molecules exhibit an intriguing behavior as a function of pump-probe delay. In particular, we observe the complete suppression of the SE and its incorporation into a large negative PA feature (650-720 nm), as well as the appearance of a well-defined derivative-shaped peak resembling an electroabsorption signal. Such an effect seems to be clearer in the less substituted molecules, and especially for the least substituted **DBOV-Ph** for which we see a progressive build-up of the electroabsorption-like signal. Conversely, if we either diluted the solutions down to 0.01 mg/mL (**Figure S5**) or embedded the molecules in a diluted PS matrix (**Figures 2b,e,h**), both the PA signal and the delayed electroabsorption are suppressed. Such behavior is thus ultimately related to the intermolecular distance experienced by the nanographenes. Therefore, we preliminary assign the derivative shape signal to a Stark shift due to charge formation, whereas the PA signal can be connected to charge absorption.²⁹ Note that we could not observe such effect in the previous study on **DBOV-Mes-C12**,²⁷ as we used a lower concentration (0.05 mg/mL) than in the work reported here. The delayed appearance of these two peaks can be linked to depopulation of the excited states (decay of the PB and SE signals) followed by the rise of the charge state. Furthermore, we reckon that one single nanographene molecule cannot sustain the formation of a stable charge population, therefore these effects occur most likely in intermolecular adducts (i.e. dimers, trimers), rather than in one single nanographene unit only. These hypotheses are corroborated by the fact that the less substituted **DBOV-Ph**, which possesses the highest tendency to form aggregates as indicated by the steady-state absorption and PLE data, exhibits the best-defined electroabsorption signal among the three molecules.

If we pass to the transient dynamics of the stimulated emission signal (**Figure 2e, f**), that is of great interest for applications of these molecules in photonic devices, we can detect a clear connection between the degree of functionalization and the photodynamic. Starting from **DBOV-Mes-C12**, the SE decay rate follows nicely the dilution series, as the signal lifetime is 400 ps for the 0.1 mg/mL solution and 1 ns for the PS film, whereas it does not decay at all for the 0.01 mg/mL solution (see **table 1** for the SE lifetimes). This can be explained in terms of the relatively high solubility of this derivative containing two dodecyl chains, which allows one to tune easily the degree of aggregation. **DBOV-Mes** displays a general decrease of the lifetime if compared to **DBOV-Mes-C12**, as well as a virtually identical photodynamic between the 0.1 and 0.01 mg/mL solutions. It is worth to note a hint of an initial ultrafast decay for this molecule that in principle can be a signature of ultrafast charge transfer processes (< 100 fs), which unfortunately we could not resolve with the temporal resolution

of our experiment (150 fs). Finally, **DBOV-Ph** solutions exhibit further lower lifetimes than the other derivatives and, despite the noise signal, in this case we can clearly discriminate an initial decay for the **DBOV-Ph** film, which loses $\approx 60\%$ of the population in 200 fs. This fast decay can be due to ultrafast charge transfer processes in the **DBOV-Ph** aggregates still present in PS dilute matrix, whereas the long decay time (1 ns) can be related to hole bleaching. These effects most probably arise from the poorer solubility of **DBOV-Ph** than that of the other molecules, both in solution and polymer matrix. We can thus conclude that the SE deactivation rate increases with decreasing bulkiness of the substituents, an effect that can be ascribed to an augmented tendency for the least substituted molecules to form aggregates with charge transfer character, in which charge generation prevails over SE.

Figure 2. (a,d,g) Transient absorption spectra as a function of pump-probe delay for DBOV-MES-C12, DBOV Mes and DBOV Ph in toluene solution (0.1 mg/mL) and (b,e,h) in PS matrix. (c,f,i) Transient dynamics for the three derivatives till 1 ns. We used an excitation wavelength of 600 nm for the solutions in toluene and 610 nm for the films in PS.

Table 1. Calculated lifetimes of the SE signal for DBOV-MES-C12, DBOV Mes and DBOV Ph.

SE lifetime	0.1 mg/mL	0.01 mg/mL	Film in PS
DBOV-Mes-C12	400 ps	Long-living	>1 ns
DBOV Mes	400 ps	1 ns	1 ns
DBOV Ph	270 ps	1 ns	$\tau_1 < 100$ fs $\tau_2 \approx 1$ ns

Finally, to gain further insights into the effect of functionalization on the optical gain properties, we performed ASE measurements on the solid films. We used a PS : nanographene 1 wt% , a ratio that we have already optimized in previous ASE experiments.²⁷ In particular, we have seen that such a concentration allows to minimize the occurrence of intermolecular charge transfer processes that would suppress gain, while maintaining a sufficient amount of material necessary for waveguiding the excitation and achieving ASE action. In agreement with the abovementioned findings, we observe a three-fold increase of the ASE threshold for the **DBOV-Mes** ($180 \mu\text{J}/\text{cm}^2$) than for **DBOV-Mes-C12** ($60 \mu\text{J}/\text{cm}^2$), whereas we could not observe any ASE action for **DBOV-Ph**. This indicates that at the same concentration the three molecules experience three different intermolecular environments which strongly depend on the presence of substituents acting as intermolecular spacers. For instance, the lack of substitution in **DBOV-Ph** leads to a stronger tendency to aggregation not only in solution, but also in the diluted polymer matrix. In these aggregates, gain and photoluminescence are quenched due to the strong competition with ultrafast charge transfer phenomena, as it has been shown in the TA section. On the other hand, although we can still observe ASE action for **DBVO-Mes**, the fluency threshold to achieve the ASE regime is higher than for **DBOV-Mes-C12**, as a result of a closer intermolecular distance in this molecule as compared with the dodecyl substituted case.

Figure 3. (a) Photoluminescence spectra taken by exciting at 620 nm (**DBOV-Mes-C12**, top graph) and 610 nm (**DBOV-Mes**, bottom graph) the films in PS (1 wt. %) with a femtosecond laser. (b) Input–output characteristics of ASE action for the 1 wt% blend in PS for **DBOV-Mes-C12** (top graph) and **DBOV-Mes** (bottom graph).

In conclusion, we have investigated the effect of peripheral functionalization on the nonlinear optical properties of three structurally defined nanographenes. Our results indicate a strong competition between optical gain and charge generation. The latter process possesses intermolecular character and thus prevails in concentrated solution and, in general, in those molecules inhibits adequate separation between the electronically active conjugated cores. For these reasons, the less substituted **DBOV-Mes** and especially **DBOV-Ph** display shorter SE lifetimes than **DBOV-Mes-C12** bearing two additional dodecyl groups. ASE measurements corroborate this scenario, as the excitation fluency threshold for achieving ASE action is three times higher in **DBOV-Mes** than **DBOV-Mes-C12**, while **DBOV-Ph** does not show any ASE. These findings can be important for selectively favoring either the light emitting or charge transport properties by simply engineering their side-group functionalities. Further studies into the photonics (i.e. lasers) and optoelectronics (light emitting diodes and solar cells) of large nanographene molecules are thus highly promising.

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Supporting Information for

Modulation of the Nonlinear Optical Properties of Dibenzo[*hi,st*]ovalene by Engineering of Peripheral Substituents

Experimental details

General:

All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under argon. Analytical thin layer chromatography (TLC) was performed on silica gel coated substrates “60 F₂₅₄” from Merck. Preparative column chromatography was performed on silica gel from Merck with a grain size of 0.063–0.200 mm (silica gel) or 0.040–0.063 mm (flash silica gel). High-resolution mass spectra (HRMS) were recorded by matrix-assisted laser decomposition/ionization (MALDI) using 7,7,8,8-tetracyanoquinodimethane (TCNQ) as matrix on a Bruker Reflex II-TOF spectrometer. Raman spectra were recorded with a Bruker RFS 100/S Raman spectrometer excited by a 488 nm laser. FT-IR spectra were obtained using a FT-IR spectrophotometer TENSOF II Bruker equipped with platinum attenuated total reflection (ATR) in the range between 400 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹. An average of 64 scans has been taken for each sample.

Materials:

Benzo[*a*]dinaphtho[2,1,8-*cde*:1',2',3',4'-*ghi*]perylene-5,14-dicarbaldehyde (**1**), **DBOV-Mes-C12**, and **DBOV-Mes** were synthesized according to the methods described in our previous reports.^{1,2} All other chemicals were purchased from commercial sources and used without further purification.

Synthesis of DBOV-Ph.

Scheme S1. Synthetic route towards DBOV-Ph.

To a solution of benzo[*a*]dinaphtho[2,1,8-*cde*:1',2',3',4'-*ghi*]perylene-5,14-dicarbaldehyde (**1**)¹ (5.0 mg, 9.9 mmol) dissolved in anhydrous tetrahydrofuran (5 mL) was added PhMgBr (0.080 mL, 0.16

mmol, 2.0 M in tetrahydrofuran). After stirring at room temperature for 2 h, the reaction was quenched by addition of saturated aqueous solution of NH_4Cl (10 mL) and extracted with ethyl acetate (10 mL) for three times. The combined organic phases were washed with brine, dried over Na_2SO_4 , and evaporated to give an orange solid, which was used for the next step without further purification. The obtained solid was dried under vacuum for 2 h and dissolved in anhydrous dichloromethane (5 mL). After addition of $\text{BF}_3\cdot\text{OEt}_2$ (0.5 mL), the solution was stirred at room temperature for 2 h under air. Methanol (20 mL) was then added and the suspension was filtered, followed by washing with dichloromethane (50 mL) to give the title compound (5 mg, 80% yield) as blue solid. Measurement of ^1H NMR was not possible even at 140 °C in *o*-dichlorobenzene (d_4) most probably because of the low solubility and strong aggregation in organic solvents. HRMS (MALDI-TOF, positive) m/z : calcd. for $\text{C}_{50}\text{H}_{24}^+$ (M) $^+$: 624.1873; found: 624.1859 (error = 2 ppm). Additional structural evidences could be obtained by comparison of FTIR, Raman, UV-VIS absorption, and PLE spectra with those of **DBOV-Mes**, which could be fully characterized by NMR in our previous report (see Figure 1 and S6).¹

Steady-state absorption and photoluminescence excitation. For the UV-VIS absorption measurements, we used a Perkin Elmer Lambda 1050 spectrophotometer, equipped with deuterium (180-320 nm) and tungsten (320-3300 nm) lamps and a photomultiplier detector (180-860 nm). All the absorption spectra were corrected for the reference spectra taken at 100% transmission (without the sample) at 0% transmission (with an internal attenuator), and for the background spectrum (toluene only or glass). The PLE spectra were taken with a Horiba Nanolog Fluorimeter, equipped with a xenon lamp, two monochromators and two detectors (photomultiplier and InGaAs).

Ultrafast pump-probe spectroscopy. For the non-degenerate pump and probe measurements, the molecules were dissolved in toluene with a concentration of 0.1 and 0.01 mg mL⁻¹. For **DBOV**: polystyrene solid blends (1% weight ratio), we dissolved the proper amount of material in a 40 mg/mL polystyrene solution in toluene (PS, Aldrich, Mw = 200,000). Then, the blends were spin-cast onto a glass substrate with a spin speed of 1000 rotations per minute yielding a thickness of $\approx$ 400 nm, as measured by profilometer. We employed an amplified Ti:sapphire laser with 2 mJ output energy, 1 kHz repetition rate and a central energy of 1.59 eV (800 nm). We used a pump wavelength of 610 nm, which is resonant with the main $\pi \rightarrow \pi^*$ transition. Such pump pulses were generated by using a visible optical parameter amplifier (OPA). Pump pulses were focused on a 200 μm spot (diameter), keeping pump fluences at $\sim$ 50 $\mu\text{J cm}^{-2}$. As a probe pulse, we used a broadband white light super-continuum generated in a sapphire plate from 450 nm to 780 nm.

Amplified spontaneous emission measurements. For ASE measurements, we employed the same films produced for pump-probe measurements. ASE characterizations were performed by using an amplified Ti:sapphire laser with 2 mJ output energy and 2 kHz repetition rate at 625 nm for **DBOV-Mes-C12** and 610 nm for **DBOV-Mes** and **DBOV-Ph**. We used a 7.5 cm cylindrical focal lens to focus the pump beam into a 2 mm $\times$ 0.1 mm strip and collected the emission from the edge of the film with a fibre spectrometer (resolution 0.5 nm).

Density functional theory calculations

Optimized geometries and simulated spectra. The DBOV molecules have been sketched with the Avogadro package.³ The optimization of the ground state geometry and the calculation of the electronic transitions have been performed with the package ORCA 3.0.3,⁴ using the B3LYP functional⁵ in the framework of the density functional theory. The Ahlrichs split valence basis set⁶ and the all-electron nonrelativistic basis set SVPalls1^{7, 8} have been employed. Moreover, the calculation utilizes the Libint library.⁹

Optimized geometries

Figure S1. Optimized geometries of **DBOV-Mes-C12**.

Figure S2. Optimized geometries of **DBOV-Mes**.

Figure S3. Optimized geometries of **DBOV-Ph**.

Absorption spectra

DBOV-Mes-C12

State	Wavelength (nm)	Oscillator strength
1	653.7	1.402510039
2	540.3	0.007853140
3	480.5	0.022907590
4	473.2	0.014948088
5	451.0	0.001972269
6	427.3	0.010790536
7	410.6	0.006305509
8	399.5	0.151176553
9	397.1	0.004598530
10	392.5	0.049129966
11	388.3	0.050020031
12	374.1	0.102582346
13	365.8	0.000944822
14	364.5	0.041416256
15	358.2	0.021301294
16	341.4	0.022966732

DBOV-Mes

State	Wavelength (nm)	Oscillator strength
1	559.4	0.963800495
2	458.0	0.000000133
3	436.8	0.001465716
4	430.2	0.000000006
5	391.3	0.000000033
6	386.6	0.000000019
7	378.0	0.000030651
8	377.8	0.000140783
9	361.1	0.175086579
10	359.9	0.004932506
11	359.7	0.011581517
12	346.2	0.123776353
13	344.6	0.000005185
14	332.8	0.009964109
15	330.3	0.000000035
16	320.6	0.051382461

DBOV-Ph

State	Wavelength (nm)	Oscillator strength
1	556.4	0.923050355

2	459.7	0.000000885
3	436.5	0.001304472
4	431.7	0.000004627
5	391.4	0.000001057
6	386.0	0.000001499
7	361.7	0.143953147
8	348.7	0.180054358
9	344.3	0.000018569
10	338.2	0.014303278
11	330.9	0.000056826
12	325.7	0.000003244
13	324.7	0.011439129
14	323.3	0.000219556
15	322.3	0.000000392
16	322.0	0.030813032

Line narrowing for the absorption: 500 cm^{-1} .

Figure 4. Absorption spectra of the DBOV molecules.

DBOV-Mes-C12 shows a red shift with respect to **DBOV-Mes** and **DBOV-Ph**. This trend agrees with the experimental absorption spectra.

XYZ coordinates of the optimized geometries

Coordinates for **DBOV-Mes-C12**
(164 atoms)

C	-0.32426014148640	-0.11820494221991	-0.13063678778650
C	-0.92693584605201	1.17936968329064	-0.14705655307724

C	-0.42435197745742	2.23501748766912	0.67042164963996
C	-1.05831594672751	3.52677797696903	0.62953953739271
C	-0.26673945339317	4.66048950206671	0.97608010060467
C	-2.42738718668177	3.59454574722689	0.10443701331813
C	-2.61646989391585	2.75447384566245	-1.04161295919871
C	-1.91994338374919	1.49544890265871	-1.10323306471384
C	-2.24208530227915	0.54284293058749	-2.11662026707481
C	-1.69801202720425	-0.77974944447132	-2.05606850897786
C	-2.08102608863805	-1.75000001057309	-3.02050804094870
C	-1.59703777494518	-3.12575524762530	-2.88504923491601
C	-0.65396494157280	-3.47842823530549	-1.85813246973215
C	-3.39990571910404	3.12199534478032	-2.18646983614917
C	-0.16207181482601	-4.84603952719199	-1.72602008369649
C	-0.20553551576296	-2.45242031130967	-0.96427503914555
C	0.83498606150775	-5.10698201954179	-0.71688892488024
C	0.77996570279539	-2.73892423833430	0.01241687575354
C	0.73910715279118	-0.38162321776585	0.79220759103486
C	0.76804338967775	2.03104369297913	1.43163578054642
C	0.94420725265105	4.44206061552583	1.64040737373772
C	1.30868761730921	-4.07166733349990	0.11367557717852
C	1.27231880300659	-1.70261432136576	0.87420033403481
C	1.28331338367146	0.66926462734042	1.58662006625319
C	1.41572884831962	3.16184001955947	1.94407767655535
C	2.34918486029556	-4.30836418251222	1.09216398094790
C	2.31172085828188	-1.97913698840352	1.81024001477775
C	2.31545274198374	0.35640083907924	2.49507751087872
C	-2.04325305218514	-4.12834225176886	-3.74477982999530
C	2.82590908793902	-3.31535370843827	1.89278533885804
C	2.80716705521528	-0.93517468763629	2.61376314508569
C	-1.59803783070966	-5.43972021870737	-3.60611987836378
C	-0.69162822330884	-5.84574712929245	-2.63032349565479
C	-2.92423289571647	-1.34224128233557	-4.07868393366129
C	-3.41118858893501	-0.04698335960668	-4.17032268219709
C	-3.10739114520465	0.91365106196070	-3.18649430564707
C	-3.60678382901522	2.25744529261071	-3.22636108898343
C	-0.75084728566642	-1.11814028674336	-1.03669379718262
H	-6.53915039213303	3.12366547227195	0.11589741550652
H	-2.03776086007194	-19.01999124815825	-5.38147085023546
H	-3.79478036538842	4.13831806861908	-2.23709580837452
H	-4.16936736813461	2.58187775946749	-4.10774295609736
H	1.55504625426313	5.30624588741231	1.92245298434452
H	2.34975247874274	3.06277304688715	2.50040930388355
H	2.76943401805687	-5.31074855842374	1.17746649717414
H	2.73111052185914	1.13789554500242	3.13401845060340
H	-2.76201820998140	-3.90733867307153	-4.53448896404783
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C	0.97502355728081	-7.28845802197696	0.55144140141453
C	2.60454704287087	-6.84117073548907	-1.21598319972105
C	1.60836940206795	-8.51654841374453	0.79034889976495
C	3.21131113351871	-8.07303702729594	-0.93818183539812

C	2.72321158481046	-8.93453771545959	0.05320115314664
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C	3.36661069988046	-10.27705462706496	0.31210488455525
C	3.16997894582188	-5.94618420494234	-2.29486923017499
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H	0.17036529979839	-6.12313550608861	2.19494121608073
H	-0.60094392586202	-7.71632425613902	1.97940047989923
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C	-1.51275891976713	-8.15860106570169	-1.89376065741761
C	-1.29169765879385	-9.67920937921466	-1.92251503467835
C	-1.44193840651663	-10.33497915444925	-3.30173437435573
C	-1.26043716899847	-11.85812033045711	-3.27718626477734
C	-1.42440696907027	-12.51687783824083	-4.65340638928264
C	-1.15279424960472	-14.02897184708746	-4.68923348689539
C	-2.15093097429897	-14.89010780031618	-3.90412963455915
C	-1.88075644031206	-16.39560104272439	-4.01698867274134
C	-2.87560677988925	-17.25799269291588	-3.22936411494658
C	-2.59891528750696	-18.76939478044566	-3.26775343807571
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H	-2.50515442492954	-7.92207832802160	-2.32439718894413
H	-1.55120850513181	-7.82381276260284	-0.84311940115531
H	-2.01505776641741	-10.14899919565028	-1.22855020493048
H	-0.28753948795111	-9.90693284291802	-1.51425081529412
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H	-2.44381062596362	-10.09418536293640	-3.71116340139062
H	-1.98227722254990	-12.29335161091913	-2.56004411698114
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H	-0.73923234456215	-12.01984373483443	-5.36685319813862
H	-2.44792183381392	-12.32171754085365	-5.03152156315825
H	-0.12843970143063	-14.22278391428519	-4.31235258811310
H	-1.15283617962303	-14.36246461186264	-5.74504386999147
H	-3.17694988799740	-14.67595507066740	-4.26534778017534
H	-2.13993265297976	-14.60331855595782	-2.83528511435926
H	-0.85368354281255	-16.60861531500683	-3.65795124780734
H	-1.89354342363805	-16.68293861678713	-5.08575335093302
H	-3.90158014026980	-17.06720403827221	-3.60401981897318
H	-2.87375240634683	-16.92473805059970	-2.17337677570977
H	-3.28271757363920	-19.26941288774409	-2.55624551792005
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H	-3.77580675592293	-19.24869878085635	-5.05146840625021
H	-2.60230262213148	-20.51144122404915	-4.59141209121050
C	-3.48653611613091	4.42238884229958	0.69518901033070
C	-4.85352768592814	4.43026983668916	0.21121676252647
C	-3.29047336655381	5.21060634651325	1.89649485448839
C	-5.68497729946212	5.51232462582643	0.52421239002502
C	-5.32470336160000	6.51206376105158	1.43349102621902
C	-4.16621031859664	6.26219142127240	2.18040828173479

C	-2.32202926166047	4.85657978585084	3.01397713191683
C	-6.19741256386817	7.71274055086316	1.69167947754226
C	-5.57324957735842	3.24025585259862	-0.40785267176531
H	-6.69415397056899	5.52374415305389	0.09655563789433
H	-3.96754988089043	6.87344713667371	3.06835630759594
H	-2.02469004155009	3.79859118540607	2.98710240281137
H	-2.83561189246964	5.03479797718409	3.97600705640243
H	-1.39571542012590	5.45165166480889	3.03306493372902
H	-7.25466183851688	7.50962228466580	1.44558097350552
H	-5.87934305292282	8.57412432680125	1.07196330448214
H	-6.14345619961288	8.03695147222693	2.74606276586919
H	-5.01673692401218	2.30019694340341	-0.28775824841220
H	-5.80522445678296	3.34897172348610	-1.48027210240849
C	-0.59445357603440	6.07428587737386	0.52060759059949
C	0.40412032051391	6.62810164077438	-0.52021249131994
C	0.44191994460320	5.85900471792872	-1.84594277932622
C	1.37531603891863	6.48881506525281	-2.88738417067743
C	1.47482231564656	5.69000177052494	-4.19305652662548
C	2.35851189658003	6.35323230462062	-5.25697293370786
C	2.50016389477885	5.53360554545855	-6.54538729611053
C	3.33671305107220	6.22483532968109	-7.62958295409945
C	3.50325103661541	5.39517732083547	-8.90837832324616
C	4.30772637117945	6.10308689786413	-10.00572523178539
C	4.48612310339896	5.27072987530812	-11.28132373713109
C	5.27549200776620	5.99304913895820	-12.37731979220536
H	-0.59911114802681	6.75986630685069	1.38813569793529
H	-1.60398530442948	6.11629873389914	0.08911097948894
H	1.42144077294942	6.65532619100451	-0.08456147612024
H	0.13124197929944	7.68291456546465	-0.71841855293848
H	-0.58247249540986	5.79629575455891	-2.26257828175780
H	0.75465723552853	4.81462494697744	-1.65716570914754
H	2.38818041219222	6.59922594946634	-2.45149828056289
H	1.03076090512607	7.51779608348920	-3.11312024488719
H	0.45877973332544	5.53767239417759	-4.60732585583240
H	1.86409876550977	4.67692394837656	-3.97090499727351
H	3.36451452019885	6.54089365316132	-4.83234929986810
H	1.94445089800679	7.35142506872136	-5.50241688738827
H	1.49307451899707	5.31147688229563	-6.94993123950733
H	2.95148578127706	4.55069312083338	-6.30492223800946
H	4.33679475167856	6.46866502612232	-7.22011349737594
H	2.86992897081918	7.19731855064648	-7.88335191039405
H	2.50321421393034	5.12986971006409	-9.30436502354780
H	3.99331072737646	4.43324431405542	-8.65849473190838
H	5.30464479638887	6.37862119937344	-9.60828550144151
H	3.81066942698220	7.06010395114495	-10.26201919394578
H	3.48996898858293	4.98601922627279	-11.67204662635848
H	4.99321269340900	4.31940622291365	-11.02788570500708
H	4.77285486812447	6.92960986179314	-12.68217123481013
H	5.38562449518545	5.36407159168203	-13.27910130306708
H	6.29036978376228	6.26117686408089	-12.03024923071176

Coordinates for **DBOV-Mes**
(92 atoms)

C	-0.81752094824052	-0.05179227598906	0.59485136327361
C	-1.51719179147868	1.20698130718531	0.51764462697142
C	-0.82742661854085	2.43358511371633	0.75506481958920
C	-1.54058680458701	3.68076474044698	0.66952160377467
C	-0.83333549901470	4.89113791544584	0.90443258081003
C	-2.93506879290497	3.69241507781421	0.35404705654683
C	-3.60720362599070	2.48406159112560	0.12503777575526
C	-2.89857092264014	1.22817328166549	0.20328795476754
C	-3.59370980870379	-0.00037499099721	-0.03798973862006
C	-2.90218357884393	-1.25134458297880	0.03668306575917
C	-3.60373702595964	-2.46866548102241	-0.20721245443724
C	-2.89049275971906	-3.74803773114481	-0.12583637872114
C	-1.49245443236795	-3.75012229725647	0.19796416218558
C	-5.01508145963050	2.45653482735887	-0.19546980903123
C	-0.77958423597992	-4.99740293243022	0.28469323750569
C	-0.80272190668127	-2.52348051677640	0.43525047069006
C	0.61463215682616	-5.00905840905158	0.60130333532882
C	0.57856355204516	-2.54467044987949	0.75009655099704
C	0.58236431282069	-0.06512917852712	0.91584669861858
C	0.57085792109901	2.43159360984402	1.07782796408517
C	0.51291120269111	4.87233768285285	1.21626340720783
C	1.28690375454176	-3.80063918798885	0.82949790017525
C	1.27380501212735	-1.31615168862314	0.99108253764674
C	1.28390180705165	1.15215819108908	1.15975398023527
C	1.20842009559650	3.65620951821355	1.30409243923025
C	2.69467816422161	-3.77313728753268	1.15032257169768
C	2.66469257081069	-1.33982046847795	1.31047340554265
C	2.65598110192499	1.08399702955551	1.47536503383643
C	-3.52775622419731	-4.97256620943158	-0.35334860758560
C	3.34794515070602	-2.60150598073075	1.38095113077991
C	3.32938602674251	-0.12534408485293	1.54941741409107
C	-2.83254778551380	-6.18883371431313	-0.26428960665373
C	-1.48686184069270	-6.20776333902928	0.04974725535621
C	-4.97604156124554	-2.40053976402560	-0.52177437579563
C	-5.64951317985156	-1.19119643283550	-0.59544211027333
C	-4.98473498681925	0.02328992457440	-0.35679293021842
C	-5.66815959901417	1.28490661621337	-0.42660794086980
C	-1.50227207946706	-1.26469473589191	0.35756604883163
C	1.35024419833850	-6.31492292258610	0.68848575864716
C	1.46794335351492	-6.98029762375047	1.92887058394536
C	1.92952020618004	-6.88183560757891	-0.47166512868269
C	2.16215198765040	-8.19870376868661	1.98756169714617
C	2.61388839315711	-8.09931995811984	-0.36702752029517
C	2.74341161805680	-8.77680649513119	0.85378110063134
C	0.86431664506173	-6.39394563276270	3.18582054958589
C	3.49018642106474	-10.08863455657714	0.93258099488598
C	1.81640407609109	-6.18962274808016	-1.81168432255577
C	-4.13451633930909	4.86878426005775	2.77029162220430
C	-5.82962419304677	8.76108887842877	0.02267816224157
C	-3.18002030615284	5.08645311596386	-2.22614964614647
C	-4.47731123336203	6.88813284064076	-1.02395024888059
C	-5.06039918168131	7.46314029426425	0.11231507545051
C	-4.93062302383412	6.78308565223295	1.32997786791928
C	-3.78696482326808	5.66902715629712	-0.96906479452836
C	-4.24843158590799	5.56232770127361	1.43100718904133
C	-3.67143865604573	4.99812992640233	0.27027165858650

H	-1.36906277763655	5.84023868205269	0.83557894193056
H	-5.55187271563222	3.40568732575160	-0.25065240029585
H	1.04540015607428	5.81090748555314	1.39793293311863
H	2.26879005774388	3.68702875510327	1.55642931131295
H	3.23143699340508	-4.72229353698204	1.20619581373728
H	3.21711654372018	1.99821255449619	1.67084539142203
H	-4.58765065444022	-5.00338136960537	-0.60764179951202
H	4.41437999063441	-2.60126277555175	1.62718355947302
H	4.39481484047628	-0.14129163882943	1.79894187386428
H	-3.36514801876752	-7.12719421859546	-0.44670363519426
H	-0.95109807712101	-7.15671531741802	0.12040531399241
H	-5.53739502567962	-3.31482465971618	-0.71631813779770
H	-6.71513263793828	-1.17530496371019	-0.84417338699538
H	-6.73465062433072	1.28456776017741	-0.67261417951051
H	2.24870901453213	-8.71021590760297	2.95234982695412
H	3.06077263627479	-8.53124709101291	-1.26937477023739
H	1.31685609887335	-5.41687693738789	3.43355287249282
H	1.01511464595742	-7.06476061270916	4.04849799009815
H	-0.22090849914453	-6.22030281278646	3.07378043955432
H	3.48608013759472	-10.49621903129596	1.95777489504072
H	4.54520188873759	-9.97129898598121	0.62162628926883
H	3.04166356761001	-10.84823418769956	0.26564937985783
H	2.34323099089520	-6.75739484657182	-2.59680423357074
H	2.24616651091025	-5.17259153755888	-1.78100301823854
H	0.76206908193375	-6.07677704085321	-2.12172598653993
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H	-3.08004716346639	4.75295394424475	3.07873083228973
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H	-5.44751969575356	9.40344215224739	-0.78990279355804
H	-5.77298101974690	9.33137046324823	0.96644931400622
H	-6.90236617310147	8.57767437048503	-0.18324201697200
H	-3.33441735510589	5.75638126250168	-3.08885531430563
H	-3.62714006247958	4.10690193717760	-2.47371433983311
H	-2.09383865525395	4.91843918806940	-2.11408406603115
H	-4.55853041068043	7.40436761128233	-1.98697381780243
H	-5.37272164844846	7.21514525279426	2.23437954606591

Coordinates for **DBOV-Ph**
(74 atoms)

C	-4.44003008021391	-3.77072354297747	-0.04020273486989
C	-3.04823707067101	-3.95110096766737	-0.02902593190755
C	-2.16997146654773	-2.86255355411663	-0.00890296645920
C	-2.71799238581052	-1.53678442916186	-0.00100445078462
C	-4.14568361286671	-1.35322659655404	-0.00351923092868
C	-4.98401356430087	-2.50074528240234	-0.02709239334093
C	-1.85785312477516	-0.39786326110412	0.00574397081715
C	-2.41619619547711	0.90411672687686	0.01274802227595
C	-3.84982336760935	1.08106675621172	0.01932910174915
C	-4.69693087994051	-0.03501163486066	0.01104407075073
C	-1.55599443587028	2.04895496408543	0.01552151050521
C	-2.12031617775775	3.35948464671945	0.02744980972394
C	-3.54860942582782	3.50888467092160	0.04374026040503
C	-4.37318074151064	2.42672464883555	0.04143440237863

C	-0.71327490253873	-3.03398618488902	0.00376527264667
C	0.13380640255528	-1.88705370447122	0.00726677830270
C	-0.42498993089193	-0.56434271669092	0.00496867010853
C	0.42498891342064	0.56433048271087	0.00498996375145
C	-0.13380703077836	1.88704178130288	0.00734505207916
C	0.71327430788996	3.03397441772602	0.00388642869096
C	0.11499743748276	4.30999617259540	0.01457352641066
C	-1.26148812382338	4.47109853398769	0.02716487878097
C	-0.11499805500319	-4.31000812381387	0.01439533713462
C	1.26148768698284	-4.47111103266352	0.02697082548352
C	2.12031561592813	-3.35949760766599	0.02729733668618
C	1.55599373513391	-2.04896719524899	0.01542760986052
C	2.41619544075481	-0.90412899821249	0.01269712169673
C	1.85785220051360	0.39785141569385	0.00574938060586
C	2.71799170874876	1.53677312079692	-0.00095720436263
C	2.16997094676599	2.86254274108593	-0.00879835430715
C	3.54860907575873	-3.50889823120324	0.04357023963906
C	4.37318060081598	-2.42673853238699	0.04130479699597
C	3.84982284706298	-1.08107925199022	0.01926229749340
C	4.69693053382057	0.03499965637638	0.01101850912269
C	4.14568302478483	1.35321584616551	-0.00348696877409
C	4.98401332501724	2.50073548554944	-0.02701696133859
C	4.44002962940793	3.77071421551499	-0.04007225604468
C	3.04823665762093	3.95109093300549	-0.02888160668690
C	-6.18467089244481	0.14404717832115	0.01758585294508
C	6.18467164461696	-0.14405886585859	0.01754636738725
C	-6.90917677823144	0.09255680300229	1.22121494347772
C	6.88792833026853	-0.36643370536407	-1.17926653929003
C	8.27627359548334	-0.53564316603408	-1.17325392488060
C	8.98518582662037	-0.48482916557637	0.03131551403574
C	8.29739137817826	-0.26215493498087	1.22880098992504
C	6.90917654899285	-0.09266468084896	1.22118059104610
C	-6.88792589413380	0.36652132990323	-1.17920956767924
C	-8.27627073631491	0.53573252873670	-1.17318504635107
C	-8.98518472891723	0.48482224951787	0.03137987591322
C	-8.29739141843082	0.26204991605490	1.22884779731603
H	-5.09527008214191	-4.64677734129433	-0.06029178692699
H	-2.66182653587747	-4.97052096849232	-0.03996242007548
H	-6.06744370241260	-2.36844445398643	-0.03728598948616
H	-3.96479997175791	4.52122905286947	0.06036488239578
H	-5.45607846761153	2.56460476194572	0.05751859675015
H	0.73740663765408	5.20574887847450	0.01551139753316
H	-1.69251417342102	5.47701620113604	0.03761344560208
H	-0.73740677248571	-5.20576112430426	0.01529930598037
H	1.69251375850357	-5.47702907164221	0.03737325956269
H	3.96479918894029	-4.52124336761837	0.06014593715524
H	5.45607886900993	-2.56461859062445	0.05737387711275
H	6.06744373415054	2.36843491953516	-0.03722012768734
H	5.09526893998324	4.64676911908773	-0.06012731084139
H	2.66182615859217	4.97051149714185	-0.03977528670204
H	-6.37510199721684	-0.08038625105032	2.16066495390385
H	6.33659412032837	-0.40814025790278	-2.12378757788377
H	8.80571050854937	-0.70991886409442	-2.11527607097133
H	10.07139749405708	-0.62046785567283	0.03725168757596
H	8.84387208862548	-0.22152553338962	2.17647774543775
H	6.37510009967794	0.08020011654944	2.16064419986707

H	-6.33659014013157	0.40830375947426	-2.12372613070022
H	-8.80570684020018	0.71008530610597	-2.11519351118387
H	-10.07139632530213	0.62046198611918	0.03732501269608
H	-8.84387298345144	0.22134622667880	2.17652094274992

Reflectance spectra for the DBOV:PS 1 wt.% films

Figure S4. Reflectance spectra of the DBOV: PS films (1 wt.% ratio).

TA spectra on 0.01 mg/mL solutions

Figure S4. TA spectra as a function of pump-probe delay for DBOV-Mes-C12 (a) DBOV-Mes (b) and DBOV-Ph (c) 0.01 mg/mL in toluene. Note the clear difference in the photodynamics among the derivatives, with DBOV-MES-C12 exhibiting the slowest dynamics even at such low concentration.

Figure S5. High-resolution mass (MALDI) spectra of **DBOV-Ph** with 7,7,8,8-tetracyanoquinodimethane (TCNQ) as matrix. The inset shows good agreement between isotopic distribution patterns of experiment and calculation.

Figure S6. (a) Raman and (b) FT-IR spectra of **DBOV-Ph** in comparison with **DBOV-Mes** (inset shows magnified spectra from 500 to 1000 cm^{-1}). The good agreement of the spectral features further corroborates the chemical identity of **DBOV-Ph**, in comparison to **DBOV-Mes**, which could be unambiguously characterized by NMR.¹

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