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Extending the Scope of Carbonyl Facilitated Triplet Excited State towards Visible Light Excitation[†]

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Abstract. A series of extended π -conjugated benzophenone analogs was synthesized through the facile Lewis-acid catalyzed Friedel-Crafts reaction in order to exploit the integral triplet state properties of benzophenone. Extending the π -conjugated plane of the phenyl ring of benzophenone allowed to tune the excitation wavelength from far-UV end (~260 nm) to the visible spectrum (~446 nm). Compared to benzophenone, significant red-shifts in the absorption (up to 450 nm in solution) with high photostability were established for the synthesized benzophenone analogs. As evident from the density functional theory calculations, expansion of ring size at the aromatic part in benzophenone analogs induces a decrease in the HOMO-LUMO gap. The considerable extension of electron density to the carbonyl group in the LUMO substantiates the triplet nature associated in the benzophenone analogs. By virtue of the properties of carbonyl functionality, an apparent increase in the triplet quantum yield ($\Phi_T = 5.4\%$ to 87.7%) was observed for benzophenone analogs when compared to the corresponding bare polyaromatic hydrocarbon. The spin orbit coupling was computationally estimated for the benzophenone analogs to propose pathways for the observed intersystem crossing process. The plausibility to photoexcite the aromatic-ring-fused benzophenone frameworks for triplet activation in the visible range opens the door for a new class of materials for photonic application.

Keywords: Benzophenone • Spin-orbit coupling • Intersystem Crossing • Triplet Excited State • Phosphorescence

Introduction

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Triplet states are important intermediates in material chemistry and invite many potential optoelectronic applications.¹ Triplet excited states of conjugated organic molecules play a major role in organic light emitting diodes (OLEDs) through harvesting of triplet excitons that enhances the electroluminescence efficiency.^{2–4} Formation of triplet excitons evade deleterious charge recombination in organic photovoltaics (OPVs).⁵⁻¹⁰ Long-lived triplet excited states can potentially give rise to larger diffusion length for advanced solar cells.¹¹ Any urge to identify conjugated organic molecules which can efficiently generate triplet states for improved performance of OLEDs, OPVs and other electronic devices can be considered noteworthy.¹²⁻¹⁵ Strategies to generate triplet excitons in conjugated organic molecules through chemical modification is still an emerging area.¹⁶⁻²¹ Incorporation of heavy atoms (such as I,^{22,23} Br,^{24,25} S,²⁶ etc.¹⁷) and auxochrome functionalities (such as carbonyl,^{27,28} nitro,^{29–31} etc.) can induce efficient triplet formation in conjugated organic molecules through enhanced spin-orbit coupling. Likewise, the out-of-plane vibrations in non-planar frameworks comprehend efficient vibronic coupling to populate the triplet excited states.³² Recent approaches have been developed to enhance triplet yield by a singlet fission process in various chromophoric systems.³³

Rapid intersystem crossing (ISC) to populate the triplet excited states in organic chromophores have been extensively investigated by time-resolved spectroscopic methods.^{34–37} In this regard, benzophenone (BP) is a prototype molecule which has been widely investigated for triplet state properties.^{38,39} A high triplet quantum yield (Φ_T) has been inferred in benzophenone which upon excitation into the singlet excited state exhibits an efficient intersystem crossing (ISC). The characteristic high triplet yield of benzophenone can classify

them as a potential photosensitizer for generating singlet oxygen in photodynamic therapy. However, benzophenone bears the ability to efficiently generate the triplet excited states by absorbing in the ultraviolet (UV) region. Incorporating the favorable property of benzophenone for efficient ISC and extending the excitation wavelength to the visible region are essential to harvest maximum photons from the solar radiation. Our longstanding interest in excited state dynamics^{40–42} prompted us to explore the triplet state properties of benzophenone through extending the conjugation at the phenyl ring and/or replacing the phenyl groups by bridging the carbonyls with π -conjugated groups (Fig. 1).



Fig. 1 Synthesis scheme and chemical structure of benzophenone (BP) analogs.

EXPERIMENTAL DETAILS

Materials and Methods

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General Informations: All chemicals were purchased from chemical suppliers and used as received, without further purification. All reactions were carried out in standard oven dried glasswares. Solvents were dried and distilled by standard procedures. TLC analyses were performed on precoated aluminum plates of silica gel 60 F254 plates (0.25 mm, Merck). IR spectra were recorded on a Shimadzu IR Prestige-21 FT-IR spectrometer as neat KBr pellets for all the derivatives. CHN analyses were carried out on an Elementar vario MICRO cube Elemental Analyzer. All values recorded in elemental analyses are given in percentage. Reference standard used for elemental analysis is 4-aminobenzenesulphonic acid (sulphanilic acid). High Resolution Mass Spectra (HRMS) was recorded on Agilent 6538 Ultra High Definition (UHD) Accurate-Mass Q-TOF-LC/MS system using either atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) mode. Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectroscopy were performed on 500 MHz and 125 MHz with Bruker AVANCE-III spectrometer respectively. Chemical shifts of ¹H NMR spectra are reported in units of parts per million (ppm) downfield from 1,1,1,1-tetramethylsilane (TMS) ($\delta = 0.0$) and relative to the signal of chloroform-d ($\delta =$ 7.260, singlet). Multiplicities were given as s (singlet); br s (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); m (multiplets), etc. The number of protons (n) for a given resonance is indicated by nH. Carbon nuclear magnetic resonance spectra (¹³C NMR) are reported in units of parts per million (ppm) downfield from 1,1,1,1-tetramethylsilane (TMS) ($\delta =$ 0.0) and relative to the signal of chloroform-d ($\delta = 77.160$, t). Absorption spectra were recorded on Shimadzu UV-3600, emission and phosphorescence on Horiba Jobin Yvon Fluorolog 3 spectrofluorimeter. The solution state fluorescence quantum yields were determined by using optically matched solutions of BP analogs and their respective standards. Quinine sulfate

dissolved in 0.5 M H₂SO₄ ($\Phi_F = 0.546$)⁴³ is used as the standard for AP, AN, PyP and PyPy; pyrene dissolved in cyclohexane ($\Phi_F = 0.32$)⁴⁴ is used as the standard for NP, NN and NN', perylene in cyclohexane ($\Phi_F = 0.94$)⁴⁴ and nile red in dioxane ($\Phi_F = 0.7$)⁴⁵ are used as reference for AA and PerP respectively.

General procedure for synthesis of BP analogs:⁴⁶ Anhydrous AlCl₃ (2 eqv.) dissolved in dry DCM was added to the stirred solution of polyaromatic hydrocarbon (Naphthalene, Anthracence, Pyrene and Perylene) in dry DCM (1 eq.) at ambient conditions. The corresponding acyl chloride (Benzoyl chloride, Naphthoyl chloride and 1-Pyrene carbonyl chloride) (1 eqv.) was then added dropwise to this stirring mixture maintained at 0° C, which is then stirred for additional 3 hours at room temperature. After the completion of the reaction, the reaction mixture was poured into 10% HCl. The resulting suspension was extracted with DCM, washed with NaHCO₃ solution, dried over Na₂SO₄ and purified through column chromatography (Silica gel, Pet ether, DCM) to afford the desired product. (For the detailed syntheses and charaterization of the BP analogs see ESI†)

Nanosecond transient absorption measurements (nTA):⁴⁰ Nanosecond laser flash photolysis experiments of the argon purged solutions were carried out in an Applied Photophysics Model LKS-60 laser kinetic spectrometer using the third harmonic (355 nm, pulse duration \approx 10 ns) of a Quanta Ray INDI-40-10 series pulsed Nd:YAG laser as the excitation source. Triplet states of BP analogs in toluene were confirmed by performing the experiments with oxygen purged solutions. Triplet quantum yields obtained upon direct photoexcitation at 355 nm were determined using [Ru(bpy)]C1₂ in methanol as standard ($\Phi_T = 100$ %), with nonsaturating laser intensities. Equal volume of 0.2 mM solution of β -carotene was added to optically matched solutions of reference and the sample. The equation for the triplet quantum yield is given by,

$$\Phi_T^s = \Phi_T^{Ref} \times \frac{\Delta A^s}{\Delta A^{Ref}} \times \frac{k_{obs}^s}{k_{obs}^s - k_0^s} \times \frac{k_{obs}^{Ref} - k_0^{Ref}}{k_{obs}^{Ref}}$$
(1)

Where, Φ_T^s and Φ_T^{Ref} denote the triplet quantum yield of the sample and reference respectively; ΔA^s and ΔA^{Ref} are transient absorption intensity of β -carotene in sample and reference respectively; k_{obs}^s and k_0^s are decay rate of sample transient species before and after the addition of β -carotene. k_{obs}^{Ref} and k_0^{Ref} are decay rate of reference transient species before and after the addition of β -carotene.

Femtosecond transient absorption technique (fTA): Spectra-physics Mai Tai Oscillator (80 MHz, 800 nm) was used as seed for a Spectra-Physics Spitfire Ace Regenerative amplifier (1 KHz, 5.5 mJ). A fraction of the amplified output was used for the generation of the 400 nm pump pulse. The residual 800 nm pulse was passed through a delay line within an Excipro pump-probe spectrometer from CDP Systems. A rotating CaF_2 plate (2 mm thickness) was used in the generation of white light from the delayed 800 nm pulses. The continuum of white light was further split into two – one as the probe and the other as the reference pulse. The transient absorption spectrum was recorded by a dual diode array detector with a detection window of 200 nm and an optical delay line resolution of 1.6 fs. The sample solution was prepared in a rotating sample cell with 1.2 mm path length. IRF was determined by solvent (10 % benzene in methanol) two photon absorption. The energy per pulse incident on the sample was attenuated employing 80% neutral density filter. fTA measurement on AP in toluene was carried out by

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exciting the sample at 400 nm, 200 nJ, ~100 fs pulses. Global analyses of the fTA spectrum was carried out using Glotaran (version 1.2).⁴⁷

X-ray Crystallography: High-quality specimens of appropriate dimensions were selected for the X-ray diffraction experiments. Crystallographic data collected are presented in the supplementary information. Single crystals were mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated Mo K α radiation. The data was collected using Bruker APEXII detector and processed using APEX2 from Bruker. All structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions, but not refined. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. The full validation of CIFs and structure factors were performed using the CheckCIF utility and found to be free of major alert level.

Computational methods: Ground-state structure optimisation, with toluene as solvent, and vibrational frequencies were computed using density functional theory (DFT) at PCM/ ω B97X-D/TVZP level of theory.^{48,49} Vertical excitation energies and oscillator strengths were calculated by employing time dependent DFT (TD-DFT) at PCM/ ω B97X-D/TVZP. All computations were performed with the Gaussian 09.⁵⁰ The spin orbit coupling was evaluated with a linear response time-dependent density functional theory using the PySOC code.⁵¹

Results and discussions

Syntheses and crystal structure analyses

Conventional Lewis acid catalyzed Friedel-Crafts aroylation at ambient conditions rendered benzophenone (BP) analogs namely naphthalen-1-yl(phenyl)methanone (NP), di(naphthalen-1naphthalen-1-yl(naphthalen-2-yl)methanone (NN'). vl)methanone (NN). anthracen-9yl(phenyl)methanone (AP), anthracen-9-yl(naphthalen-1-yl)methanone (AN), di(anthracen-9yl)methanone (AA), phenyl(pyren-1-yl)methanone (PyP), di(pyren-1-yl)methanone (PyPy) and perylen-3-yl(phenyl)methanone (PerP) with moderate to high yields (31-75 %) (Fig. 1). Single crystals of NP, NN, NN', AN, AA and PyP suitable for X- ray diffraction (XRD) analysis were obtained through slow evaporation of hexane/chloroform mixtures at ambient conditions. The XRD analysis of NN, NN', AA established the formation of solvent free monoclinic crystal system with space group $P2_1/n$, $P2_1$, and $P2_1/c$ respectively, whereas NP and AN crystallized in orthorhombic crystal system with $P2_12_12_1$ and $Pca2_1$ space groups. PyP exhibited a solvent free triclinic crystal system with P-1 space group (Fig. 2, Table S1; ESI⁺). The dihedral angle between the carbonyl group and the corresponding arenes in NN, NN' and AA crystals is 17.9°, 21.2° and 46.5° respectively (Fig. S1; ESI⁺). Compounds containing dissimilar arenes displayed two torsional angles with respect to the carbonyl group. Torsional angles of 67.3° and 25.6° were identified for crystalline AN relative to the carbonyl group which could be due to the twist of anthracene and naphthalene respectively.



Fig. 2 Single crystal X-ray structure of I) NP, II) PyP, II) NN, IV) NN', V) AN, VI) AA.

Steady state absorption, emission and frontier molecular orbital analyses

UV-Vis absorption spectra of BP analogs (Fig. 3, Fig. S2 & Table S2; ESI[†]) were recorded in toluene. The absorption maxima of the BP analogs spanned from the UV region, 305 nm for NP, to the visible region, 446 nm for PerP. A significant red-shift of ~141 nm observed in the absorption maximum of PerP relative to NP could be attributed to the extension in the π conjugation of the benzophenone core.



Fig. 3 UV-Vis absorption spectra of BP analogs in toluene.

Density functional theory (DFT) calculations were performed to correlate the observed redshift in the electronic absorption spectrum (Table S3 and Fig. S3; ESI†). Though marginally blue-shifted with respect to the experimental data, the calculated λ_{max} agree well with the trend observed in the experimental data with increase in the size of the aromatic core. The vertical excitation energies computed from the TD-DFT calculation revealed that the first vertical transition (S₀ \rightarrow S₁) is described by HOMO \rightarrow LUMO excitation, with appreciable oscillator strength in the presented benzophenone analogs (f = 0.0123-0.7110; see Fig. 4C and Table S4; ESI†). Careful analysis of the frontier molecular orbitals indicates that the LUMO is more delocalized with modest extension to the carbonyl group, while a significant electron density on oxygen atom of the carbonyl group hint towards the non-bonding nature of the molecular orbital. (Fig. 4A and 4B, Fig. S4 & S5; ESI†). The low-intensity short wavelength band (HOMO \rightarrow LUMO) emerge as a result of n- π * transition of the carbonyl group. The prominent long wavelength bands were assigned to have contributions from π - π * transition.

Fluorescence spectra recorded on photoexcitation of BP analogs in toluene at 305-450 nm, exhibited emission bands centered at around 380-630 nm (Table 1, Fig. S6; ESI†). The solution state fluorescence quantum yield (Φ_F) of the BP analogs were determined using optically matched solutions of the sample and the respective standards (see experimental details). The estimated ϕ_F using pyrene in cyclohexane as the reference ($\Phi_F = 32\%$)⁴⁴ for NP, NN, NN' were 1.9, 2.1 and 0.9 % respectively. Similarly AP, AN, PyP and PyPy demonstrated a Φ_F of 0.3, 0.2, 2.7 and 25.3 % respectively, by matching with quinine sulphate in 0.05 M H₂SO₄ ($\Phi_F =$ 54.6%).⁴³ Perylene in cyclohexane ($\Phi_F = 94\%$)⁴⁴ was used as a reference to measure the Φ_F of AA and the obtained quantum yield was 1.7%. The highest fluorescence quantum yield among the BP analogs was exhibited by PerP with Φ_F of 35%, quantified using nile red in dioxane ($\Phi_F =$



Fig. 4 The frontier molecular orbitals A) HOMO B) LUMO of PerP; C) Energy level diagram for BP analogs as calculated using TD-DFT (PCM/ωB97X-D/TZVP).

Nanosecond transient absorption measurements

In order to get insights into the intrinsic triplet character of benzophenone upon π conjugation, nanosecond transient absorption measurements (nTA) of the BP analogs in toluene were carried out by exciting the samples at 355 nm (Fig. 5 and Fig. S7; ESI†). Upon photoexcitation ($\lambda_{exc} = 355$ nm), BP analogs NP, NN, and NN' exhibited positive absorption peaks in the spectral region 450 nm to 600 nm. The observed band corresponds to the triplettriplet absorption and is in excellent agreement with the naphthalene T₁ transition.⁵² Crespo-Hernández and co-workers have identified a similar observation in the nanosecond broadband transient absorption of nitronaphthalene derivatives.²⁹ Observed triplet band exhibited a lifetime (τ_{T}) of 0.2, 0.3 and 0.3 µs for NP, NN and NN' respectively (Table 1, Fig. S8; ESI†). Triplet quantum yield (Φ_T) measurement of BP analogs were performed by employing triplet-triplet energy transfer method using β -carotene as a triplet sensitizer.⁵³ The calculated Φ_T values were 60.1, 87.6 and 63.4% for NP, NN and NN' respectively (Table 1). The nTA measurements on AP, AN and AA displayed absorption maximum at around 430-450 nm (Fig. 5 & S7; ESI†). A pronounced negative absorption was observed at 350 nm, corresponding to the steady state absorption of anthracene (A) unit which manifests the ground state depopulation of A. The transient absorption

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Fig. 5 nTA spectra of A) AA, B) AP and C) PyPy in toluene with the respective kinetic traces monitored at 450 nm ($\lambda_{ex} = 355$ nm).

Table 1. Triplet lifetime (τ_T) and triplet quantum yield (Φ_T) in toluene using triplet-triplet energy transfer method.

	Compound	Φ_F^a (%)	$ au_{T}^{b}(\mu s)$	$\Phi_T^c(\%)$	Φ_T^d (%)
	BP	~ 0	10	100	57 ⁵⁴
	NP	1.9	0.2	60.1	
	NN	2.1	0.3	87.6	80^{55}
	NN'	0.9	0.3	63.4	
	AP	0.3	0.7	86.7	
	AN	0.2	0.9	75.8	72 ⁵⁵
	AA	1.7	1.1	77.4	
	РуР	2.7	1.8	ך 48.2	2055
	PyPy	25.3	2.6	69.2	38
	PerP	35.0	1.9	5.4	~ 0
^a fluorescence quantum yield; ^b triplet life time; ^c triplet quantum yield					
	of correspondir	ng BP an	alogs. ^d triplet	quantum	yield of bare

chromophore taken from literatures.

signals observed around 430-450 nm were readily quenched by the dissolved oxygen which strongly suggests the existence of triplet excited state (${}^{3}A^{*}$; Fig. S9; ESI†). The positive absorption band around 430-450 nm thus, could be due to the triplet absorption of anthracene (${}^{3}A^{*}$)⁵⁶ possessing triplet lifetime (τ_{T}) of 0.7, 0.9 and 1.1 µs for AP, AN and AA, respectively (Fig. 5, Table 1 & Fig. S8; ESI†). Estimated quantum yields of 86.7, 75.8 and 77.4%, respectively for the aroylated anthracene, showed 5-20% enhancement in Φ_{T} compared to the corresponding bare chromophore, A ($\Phi_{T} = 72\%$). Similar features of triplet absorption were observed in pyrene containing analogs, PyP and PyPy with absorption maximum at 500-520 nm and triplet lifetime of 1.8 and 2.6 µs respectively (Fig. 5, Table 1 & Fig. S7; ESI†). The absorption band at 500-520 nm could be attributed to the triplet absorption of pyrene (${}^{3}Py^{*}$) with Φ_{T} of 48.2% (PyP) and 69.2% (PyPy). The estimated ϕ_{T} for pyrene containing analogs exhibited an increase in the triplet quantum yield by 27-82% than the bare pyrene which has a reported triplet quantum yield of 38% (Φ_{T}). PerP was characterized by a weak transient absorption band at 500 nm with life time of 1.9 µs and Φ_{T} of 5.4% (Table 1, Fig. S7; ESI†). The corresponding bare chromophore, perylene exhibits negligible triplet quantum yield.

Triplet formation by visible light excitation

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The concrete evidence for visible light excitation populating the triplet states in the BP analogs was provided by femtosecond transient absorption (fTA) spectroscopy (Fig. 6A-C). The representative PyP ($\Phi_T = 69.2\%$) was photoexcited at 400 nm using 100 fs laser pulse. The transient absorption band for PyP in toluene initially decaying at 530 nm indicates the absorption of the higher energy singlet state ($S_2 \rightarrow S_n$ transition), as reported by Foggi and co-workers.⁵⁷ The decay of the peak at 530 nm is followed by the appearance of a singlet excited state (S_1) corresponding to the absorption band at 460 nm ($S_1 \rightarrow S_m$ transition).¹⁸ The singlet state S_1 then undergoes ISC process to populate the triplet state (T_n) represented by the absorption peak at 510 nm.^{18,42}

Time-gated emission measurements

To better understand the emissive nature of the triplet states, time-gated emission measurement of BP analogs was performed by photoexciting the deoxygenated ethanolic solutions at the respective absorption maxima. The emission profile obtained at 77 K for NN and NN' after a delay time of 0.05 ms were red shifted (ca. 130-150 nm; Fig. 6D) when compared to their fluorescence spectra. While, the spectral profile of AA, PyPy and PerP at 77 K obtained

after a 0.05 ms delay matched their respective fluorescence emission spectra.⁵⁸ Radiative decay of the triplet excited states has been reported in the cases of BP and NP whereas AP and PyP exhibit no phosphorescence.⁵⁹ The phosphorescence spectra of NN' range from 475 nm to 675 nm and that of NN span from 475 nm to 650 nm (Fig. 6D).



Fig. 6 Shows the A) fTA spectrum of PyP in toluene upon excitation at 400 nm; B) Evolution associated spectra corresponding to the spectra shown in Fig. 6A; C) population profile of spectra shown in Fig. 6A; D) phosphorescence emission spectra of NN and NN' in ethanol.

Triplet populating pathways and spin orbit coupling

To gain insight into the pathways populating the triplet manifolds in BP analogs via the spin orbit coupling (SOC) mechanism,^{60,61} the SOCs were calculated using the PySOC code developed by Thiel and co-workers.⁵¹ The SOCs were evaluated at the Franck-Condon geometry. In BP, the large SOC value (Table S5; ESI⁺) for S_1/T_1 (13 cm⁻¹) and a significant SOC for S_1/T_2 (3 cm⁻¹) could efficiently populate the triplet manifold by the ultrafast ISC process as reported.³⁸ A similar pathway for populating the triplet could exist in the other carbonyl derivatives, however, governed by El-Sayed's rule.⁶² $S_1 \rightarrow T_2 \rightarrow T_1$ or $S_1 \rightarrow T_3 \rightarrow T_1$ could be the pathway populating the triplet in NP. The SOC for S_1/T_2 (10 cm⁻¹) or S_1/T_3 (12 cm⁻¹) could be sufficient for promoting the ISC in NP. The near degenerate S_1 and T_4 with a SOC of 11 cm⁻¹ and 9 cm⁻¹ in NN and NN' respectively could allow ISC to generate the triplet states (Fig. S10; ESI[†]). In AP, quasi-degenerate $T_2/T_3/T_4$ and a small ΔE_{S-T} (0.1-0.2 eV) could promote the population of the triplet states from S₁. The lower triplet quantum yield in AN and AA, in comparison to AP, could be attributed to the low SOCs in the range of 0.3 cm⁻¹ to 5 cm⁻¹ for S_1/T_3 and S_1/T_4 respectively. Despite the low SOC between the states, a small value of ΔE_{S-T} could promote the ISC process in AN and AA. In case of PyP and PyPy, the $S_1 \rightarrow T_4$ pathway could dominate the ISC process. However, the nature of the $S_1 \rightarrow T_4$ transition is allowed in PyPy, $S_1(n-\pi^*) \rightarrow T_4(\pi-\pi^*)$ and forbidden in PyP, $S_1(n-\pi^*) \rightarrow T_4(n-\pi^*)$, which could explain the lower triplet quantum yield in PyP compared to PyPy (Fig. S10; ESI⁺). Similarly, the low quantum yield of triplet in PerP could be attributed to a low SOC for S_1/T_2 and also the forbidden nature of the S_1/T_2 transition. In addition, the deviation from planarity observed in the BP analogs could considerably alter the ISC process in such systems.⁶³

Conclusions

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In conclusion, visible light-harvesting benzophenone analogs that can be used as organic triplet generators were designed and synthesized through a facile aroylation reaction. Efforts to extend the π -conjugation of the phenyl ring(s) on benzophenone (BP) allowed to tune the photoabsorption from UV to the visible region. Considerable expansion in the π -conjugation of the phenyl ring led to a 186 nm (e.g. PerP) red shifted absorption when compared to that of BP, which is corroborated by DFT calculations. Population of long-lived triplet excited states were confirmed by nanosecond time resolved absorption which exhibited an increase in the triplet quantum yield in BP analogs ($\Delta \Phi_T = 5.4$ to 31.2%) when compared to their respective bare polyaromatic hydrocarbons. The visible light excitation populating the triplet excited states in the BP analogs was confirmed by femtosecond time-resolved absorption spectroscopic technique. Furthermore, the computationally predicted spin orbit couplings in the BP analogs aid in proposing the triplet population pathways that substantiates with the experimentally observed trends in triplet quantum yield. Though the analogs have a lower triplet quantum yield than the parent BP, the strategy of multiple aroylation of the BP analogs could possibly increase the triplet quantum yield and also result in the red-shift of the UV-Vis absorption of the analogs, as observed earlier.⁴² The enhanced triplet activation through photoexcitation in the visible range in benzophenone analogs will thus make them desirable materials for triplet excitons generators for organic photovoltaic devices.

[†]Electronic Supplementary Information (ESI) available: Experimental details, ¹H and ¹³C NMR spectra of BP analogs as well as characterization data. Computational details, fluorescence and nanosecond time-resolved spectra for BP analogs. CCDC 1559462-1559466, 1440151.
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Notes and references

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- 1 S. K. Lower and M. A. El-Sayed, The Triplet State and Molecular Electronic Processes in Organic Molecules, *Chem. Rev.*, 1966, **66**, 199–241.
- 2 M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, Highly efficient phosphorescent emission from organic electroluminescent devices, *Nature*, 1998, **395**, 151–154.
- R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund and W. R. Salaneck, Electroluminescence in conjugated polymers, *Nature*, 1999, **397**, 121–128.
- 4 A. Köhler and H. Bässler, Triplet states in organic semiconductors, *Mater. Sci. Eng. R Reports*, 2009, **66**, 71–109.
- 5 G. Lakhwani, A. Rao and R. H. Friend, Bimolecular Recombination in Organic Photovoltaics, *Annu. Rev. Phys. Chem.*, 2014, **65**, 557–581.
- 6 A. Rao, P. C. Y. Chow, S. G??linas, C. W. Schlenker, C. Z. Li, H. L. Yip, A. K. Y. Jen, D.

S. Ginger and R. H. Friend, The role of spin in the kinetic control of recombination in organic photovoltaics, *Nature*, 2013, **500**, 435–439.

- S. Westenhoff, I. A. Howard, J. M. Hodgkiss, K. R. Kirov, H. A. Bronstein, C. K. Williams, N. C. Greenham and R. H. Friend, Charge Recombination in Organic Photovoltaic Devices with High Open-Circuit Voltages, J. Am. Chem. Soc., 2008, 130, 13653–13658.
- 8 Y. Shao and Y. Yang, Efficient Organic Heterojunction Photovoltaic Cells Based on Triplet Materials, *Adv. Mater.*, 2005, **17**, 2841–2844.
- 9 S. R. Yost, E. Hontz, S. Yeganeh and T. Van Voorhis, Triplet vs Singlet Energy Transfer in Organic Semiconductors: The Tortoise and the Hare, *J. Phys. Chem. C*, 2012, **116**, 17369–17377.
- 10 H. Ohkita, S. Cook, Y. Astuti, W. Duffy, M. Heeney, S. Tierney, I. McCulloch, D. D. C. Bradley and J. R. Durrant, Radical ion pair mediated triplet formation in polymer-fullerene blend films, *Chem. Commun.*, 2006, 0, 3939–3941.
- 11 M. J. Y. Tayebjee, A. A. Gray-Weale and T. W. Schmidt, Thermodynamic Limit of Exciton Fission Solar Cell Efficiency, *J. Phys. Chem. Lett.*, 2012, **3**, 2749–2754.
- 12 E. R. Bittner, V. Lankevich, S. Gelinas, A. Rao, D. A. Ginger and R. H. Friend, How disorder controls the kinetics of triplet charge recombination in semiconducting organic polymer photovoltaics, *Phys. Chem. Chem. Phys.*, 2014, **16**, 20321–20328.
- 13 J. Zhao, K. Xu, W. Yang, Z. Wang and F. Zhong, The triplet excited state of Bodipy: formation, modulation and application, *Chem. Soc. Rev.*, 2015, **44**, 8904–8939.
- 14 J.-S. Yang and C.-J. Lin, Fate of photoexcited trans-aminostilbenes, J. Photochem. *Photobiol. A Chem.*, 2015, **312**, 107–120.
- 15 J. A. Sanchez-Rodriguez, A. Mohamadzade, S. Mai, B. Ashwood, M. Pollum, P. Marquetand, L. Gonzalez, C. E. Crespo-Hernandez and S. Ullrich, 2-Thiouracil intersystem crossing photodynamics studied by wavelength-dependent photoelectron and transient absorption spectroscopies, *Phys. Chem. Chem. Phys.*, , DOI:10.1039/C7CP02258A.
- 16 N. Adarsh, M. Shanmugasundaram, R. R. Avirah and D. Ramaiah, Aza□BODIPY Derivatives: Enhanced Quantum Yields of Triplet Excited States and the Generation of Singlet Oxygen and their Role as Facile Sustainable Photooxygenation Catalysts, *Chem. Eur. J.*, 2012, **18**, 12655–12662.
- 17 P. Spenst, R. M. Young, M. R. Wasielewski and F. Wurthner, Guest and solvent modulated photo-driven charge separation and triplet generation in a perylene bisimide cyclophane, *Chem. Sci.*, 2016, 7, 5428–5434.
- 18 R. A. Vogt, M. A. Peay, T. G. Gray and C. E. Crespo-Hernández, Excited-State Dynamics of (Organophosphine)gold(I) Pyrenyl Isomers, *J. Phys. Chem. Lett.*, 2010, 1, 1205–1211.
- 19 S. Jockusch, M. Porel, V. Ramamurthy and N. J. Turro, CIDEP from a Polarized Ketone Triplet State Incarcerated within a Nanocapsule to a Nitroxide in the Bulk Aqueous Solution, *J. Phys. Chem. Lett.*, 2011, **2**, 2877–2880.
- 20 A. I. Burshtein and K. L. Ivanov, The crucial role of triplets in photoinduced charge transfer and separation, *Phys. Chem. Chem. Phys.*, 2002, **4**, 4115–4125.
- 21 M. C. Sajimon, D. Ramaiah, C. H. Suresh, W. Adam, F. D. Lewis and M. V George, Photochromic Dibenzobarrlenes: Long-Lived Triplet Biradical Intermediates, *J. Am. Chem. Soc.*, 2007, **129**, 9439–9445.
- 22 S. Henkel, P. Costa, L. Klute, P. Sokkar, M. Fernandez-Oliva, W. Thiel, E. Sanchez-

Garcia and W. Sander, Switching the Spin State of Diphenylcarbene via Halogen Bonding, J. Am. Chem. Soc., 2016, **138**, 1689–1697.

- 23 C. Zhang and J. Zhao, Triplet excited state of diiodoBOPHY derivatives: preparation, study of photophysical properties and application in triplet-triplet annihilation upconversion, *J. Mater. Chem. C*, 2016, **4**, 1623–1632.
- G. G. Giachino and D. R. Kearns, Nature of the External Heavy Atom Effect on Radiative and Nonradiative Singlet–Triplet Transitions, J. Chem. Phys., 1970, 52, 2964–2974.
- H. Saigusa and T. Azumi, Internal heavy atom effect on the triplet spin sublevels of the lowest triplet state of naphthalene. I. Radiative and nonradiative decays of the spin sublevels of 1 □ halonaphthalenes, J. Chem. Phys., 1979, 71, 1408–1413.
- 26 Y. Chen, J. Zhao, L. Xie, H. Guo and Q. Li, Thienyl-substituted BODIPYs with strong visible light-absorption and long-lived triplet excited states as organic triplet sensitizers for triplet-triplet annihilation upconversion, *RSC Adv.*, 2012, **2**, 3942–3953.
- 27 Y. Niko, Y. Hiroshige, S. Kawauchi and G. Konishi, Additional Insights into Luminescence Process of Polycyclic Aromatic Hydrocarbons with Carbonyl Groups: Photophysical Properties of Secondary N-Alkyl and Tertiary N,N-Dialkyl Carboxamides of Naphthalene, Anthracene, and Pyrene, J. Org. Chem., 2012, 77, 3986–3996.

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- H. J. van Ramesdonk, B. H. Bakker, M. M. Groeneveld, J. W. Verhoeven, B. D. Allen, J. P. Rostron and A. Harriman, Ultrafast Intersystem Crossing in 9,10-Anthraquinones and Intramolecular Charge Separation in an Anthraquinone-Based Dyad, *J. Phys. Chem. A*, 2006, 110, 13145–13150.
- 29 R. A. Vogt, C. Reichardt and C. E. Crespo-Hernández, Excited-State Dynamics in Nitro-Naphthalene Derivatives: Intersystem Crossing to the Triplet Manifold in Hundreds of Femtoseconds, J. Phys. Chem. A, 2013, 117, 6580–6588.
- 30 S. Murudkar, A. K. Mora, P. K. Singh and S. Nath, Origin of Ultrafast Excited State Dynamics of 1-Nitropyrene, *J. Phys. Chem. A*, 2011, **115**, 10762–10766.
- 31 J. S. Zugazagoitia, E. Collado-Fregoso, E. F. Plaza-Medina and J. Peon, Relaxation in the Triplet Manifold of 1-Nitronaphthalene Observed by Transient Absorption Spectroscopy, J. Phys. Chem. A, 2009, **113**, 805–810.
- 32 X. Cheng, F. Li, S. Han, Y. Zhang, C. Jiao, J. Wei, K. Ye, Y. Wang and H. Zhang, Emission behaviors of unsymmetrical 1,3-diaryl-β-diketones: A model perfectly disclosing the effect of molecular conformation on luminescence of organic solids, *Sci. Rep.*, 2015, 5, 9140.
- 33 M. B. Smith and J. Michl, Singlet Fission, *Chem. Rev.*, 2010, **110**, 6891–6936.
- 34 Y. Harada, C. Okabe, T. Kobayashi, T. Suzuki, T. Ichimura, N. Nishi and Y. Z. Xu, Ultrafast Intersystem Crossing of 4-Thiothymidine in Aqueous Solution, *J. Phys. Chem. Lett.*, 2010, **1**, 480–484.
- 35 M. Richter, P. Marquetand, J. González-Vázquez, I. Sola and L. González, Femtosecond Intersystem Crossing in the DNA Nucleobase Cytosine, *J. Phys. Chem. Lett.*, 2012, **3**, 3090–3095.
- 36 R. P. Sabatini, T. M. McCormick, T. Lazarides, K. C. Wilson, R. Eisenberg and D. W. McCamant, Intersystem Crossing in Halogenated Bodipy Chromophores Used for Solar Hydrogen Production, *J. Phys. Chem. Lett.*, 2011, **2**, 223–227.
- 37 O. Yushchenko, G. Licari, S. Mosquera-Vazquez, N. Sakai, S. Matile and E. Vauthey, Ultrafast Intersystem-Crossing Dynamics and Breakdown of the Kasha–Vavilov's Rule of

Naphthalenediimides, J. Phys. Chem. Lett., 2015, 6, 2096–2100.

- 38 M. Marazzi, S. Mai, D. Roca-Sanjuán, M. G. Delcey, R. Lindh, L. González and A. Monari, Benzophenone Ultrafast Triplet Population: Revisiting the Kinetic Model by Surface-Hopping Dynamics, *J. Phys. Chem. Lett.*, 2016, 7, 622–626.
- 39 S. Aloïse, C. Ruckebusch, L. Blanchet, J. Réhault, G. Buntinx and J. P. Huvenne, The benzophenone $S1(n,\pi^*) \rightarrow T1(n,\pi^*)$ states intersystem crossing reinvestigated by ultrafast absorption spectroscopy and multivariate curve resolution, *J. Phys. Chem. A*, 2008, **112**, 224–231.
- 40 K. Nagarajan, A. R. Mallia, V. S. Reddy and M. Hariharan, Access to Triplet Excited State in Core-Twisted Perylenediimide, *J. Phys. Chem. C*, 2016, **120**, 8443–8450.
- 41 A. M. Philip, A. R. Mallia and M. Hariharan, Prolonged Charge Separated States in Twisted Stacks of All-Carbon Donor and Acceptor Chromophores, *J. Phys. Chem. Lett.*, 2016, 7, 4751–4756.
- 42 S. K. Rajagopal, A. R. Mallia and M. Hariharan, Enhanced intersystem crossing in carbonylpyrenes, *Phys. Chem. Chem. Phys.*, 2017, **19**, 28225–28231.
- 43 D. F. Eaton, No Title, *Pure Appl. Chem.*, 1988, **60**, 1107 1114.
- 44 I. B. Berlman, in *Handbook of Fluorescence Spectra of Aromatic Molecules (Second Edition)*, Academic Press, 1971, pp. 107–415.
- 45 D. L. Sackett and J. Wolff, Nile red as a polarity-sensitive fluorescent probe of hydrophobic protein surfaces, *Anal. Biochem.*, 1987, **167**, 228–234.
- 46 H. Vollmann, H. Becker, M. Corell and H. Streeck, Beiträge zur Kenntnis des Pyrens und seiner Derivate, *Justus Liebigs Ann. Chem.*, 1937, **531**, 1–159.
- 47 J. J. Snellenburg, S. P. Laptenok, R. Seger, K. M. Mullen and I. H. M. van Stokkum, Glotaran : A Java -Based Graphical User Interface for the R Package TIMP, *J. Stat. Softw.*, 2012, **49**, 1–22.
- 48 J.-D. Chai and M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615.
- 49 A. Schäfer, C. Huber and R. Ahlrichs, Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr, *J. Chem. Phys.*, 1994, **100**, 5829–5835.
- 50 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson and E. Al., *Gaussian 09, revision* A.02, 2009.
- 51 X. Gao, S. Bai, D. Fazzi, T. Niehaus, M. Barbatti and W. Thiel, Evaluation of Spin-Orbit Couplings with Linear-Response Time-Dependent Density Functional Methods, *J. Chem. Theory Comput.*, 2017, **13**, 515–524.
- 52 X. Cai, M. Hara, K. Kawai, S. Tojo and T. Majima, Naphthalene in the higher triplet excited state, *Chem. Commun.*, 2003, 222–223.
- 53 C. V Kumar, L. Qin and P. K. Das, Aromatic thioketone triplets and their quenching behaviour towards oxygen and di-t-butylnitroxy radical. A laser-flash-photolysis study, *J. Chem. Soc. Faraday Trans. 2 Mol. Chem. Phys.*, 1984, **80**, 783–793.
- 54 R. B. Cundall and W. Tippett, Intersystem crossing in irradiated benzene and toluene, *Trans. Faraday Soc.*, 1970, **66**, 350–362.
- 55 A. R. Horrocks and F. Wilkinson, Triplet State Formation Efficiencies of Aromatic Hydrocarbons in Solution, *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.*, 1968, **306**, 257–273.
- 56 E. J. Land, Absorption spectrum of the triplet state of duroquinone, Trans. Faraday Soc.,

1969, 65, 2815-2822.

- 57 F. V. R. Neuwahl and P. Foggi, Direct Observation of S₂ –S₁ Internal Conversion in Pyrene by Femtosecond Transient Absorption, *Laser Chem.*, 1999, **19**, 375–379.
- 58 S. Y. Lee, T. Yasuda, Y. S. Yang, Q. Zhang and C. Adachi, Luminous Butterflies: Efficient Exciton Harvesting by Benzophenone Derivatives for Full-Color Delayed Fluorescence OLEDs, *Angew. Chemie Int. Ed.*, 2014, **53**, 6402–6406.
- 59 C. Parkanyi, E. J. Baum, J. Wyatt and J. N. Pitts, Physical properties and chemical reactivity of alternant hydrocarbons and related compounds. XVI. Electronic absorption and phosphorescence spectra of aryl phenyl ketones, *J. Phys. Chem.*, 1969, **73**, 1132–1138.
- N. Ohmori, T. Suzuki and M. Ito, Why does intersystem crossing occur in isolated molecules of benzaldehyde, acetophenone, and benzophenone?, *J. Phys. Chem.*, 1988, **92**, 1086–1093.
- 61 S. Yabumoto, S. Sato and H. Hamaguchi, Vibrational and electronic infrared absorption spectra of benzophenone in the lowest excited triplet state, *Chem. Phys. Lett.*, 2005, **416**, 100–103.
- 62 M. A. El-Sayed, Triplet state. Its radiative and nonradiative properties, *Acc. Chem. Res.*, 1968, **1**, 8–16.
- K. Schmidt, S. Brovelli, V. Coropceanu, D. Beljonne, J. Cornil, C. Bazzini, T. Caronna, R. Tubino, F. Meinardi, Z. Shuai and J. L. Brédas, Intersystem crossing processes in nonplanar aromatic heterocyclic molecules, *J. Phys. Chem. A*, 2007, 111, 10490–10499.

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