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Highly luminescent, polyaryl mesobenzanthrones

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ABSTRACT

Several highly luminescent, aryl-substituted mesobenzanthrones (7*H*-benz[*de*]anthracen-7-ones) were prepared by a simple, two-step synthesis: addition of a carboxylated benzyne to a cyclopentadienone followed by an intramolecular Friedel–Crafts acylation. These compounds exhibit brilliant, yellow-green luminescence with quantum yields ranging from 0.01 to 1, depending on the aryl substituents present, and their photophysical behavior was elucidated by experimental and computational methods.

1. Introduction

We have previously reported the synthesis of several cleft-containing, polyphenyl aromatic compounds, dubbed the 'albatrossenes' (**1**, Scheme 1),[1,2] by the addition of tetraphenylbenzyne (generated by the diazotization of tetraphenylanthranilic acid[3]) to biscyclopentadienones (**2**). In an attempt to functionalize the clefts with more highly polar groups, 3-aminophthalic acid (**4**) was substituted as the aryne precursor, but the reaction led instead to a complex mixture containing several highly luminescent products. The precise identity of these materials is uncertain, but their likely nature was illuminated by a model reaction. Diazotization of **4** in the presence of tetracyclone (**6**), followed by a workup that included an aqueous HCl wash of the organic products, led to the formation of 1,2,3-triphenylmesobenzanthrone (**8**, 1,2,3-triphenyl-7*H*-benz[*de*]anthracen-7-one), a yellow compound with a brilliant, yellow-green luminescence.

The photophysics of simple, monosubstituted mesobenzanthrones has been well studied,[4-6] but no polyaryl mesobenzanthrones have been reported previously. With such a short synthesis in hand, and encouraged by the seemingly unquenchable thirst for new organic lumiphores with applications in biological and materials sciences,[7–10] the further investigation of this new class of fluors seemed appropriate. We now report the synthesis and photophysics of a short series of polyaryl mesobenzanthrones.

2. Results and discussion

2.1. Synthesis and structure

In the original synthesis of **8**, the addition of 3-carboxybenzyne (derived from **4**) to tetracyclone, followed by loss of carbon monoxide, gives the expected intermediate 5,6,7,8-tetraphenyl-1-naphthoic acid (**7**), but due to the proximity of the 1-carboxyl and 8-phenyl groups, even aqueous acid is sufficient to catalyze an intramolecular Friedel–Crafts acylation. However, this synthesis suffers from extremely poor yields (typically less than 5%) due to the interference of free carboxylic acids with aryne additions.

Fortunately, the half ester of compound **4**, 2-amino-6-(methoxycarbonyl)benzoic acid (**9**, Scheme 2) is known.[11] Its diazotization yields 3-methoxycarbonylbenzyne, which adds readily to cyclopentadienones without complications. The resulting adduct only slowly undergoes the intramolecular Friedel–Crafts acylation in the presence of aqueous HCl, but if the adduct is instead heated with thionyl chloride in toluene, the desired mesobenzanthrone forms easily. The intermediate ester need not be isolated. It is only necessary to carry out an ordinary aqueous workup of the aryne addition, strip the solvent from the organic extract, and heat this material in toluene with a small amount of thionyl chloride. In this way, 1,2,3-triphenylmesobenzanthrone (**8**) was prepared in 41% yield from tetracyclone (**6**).

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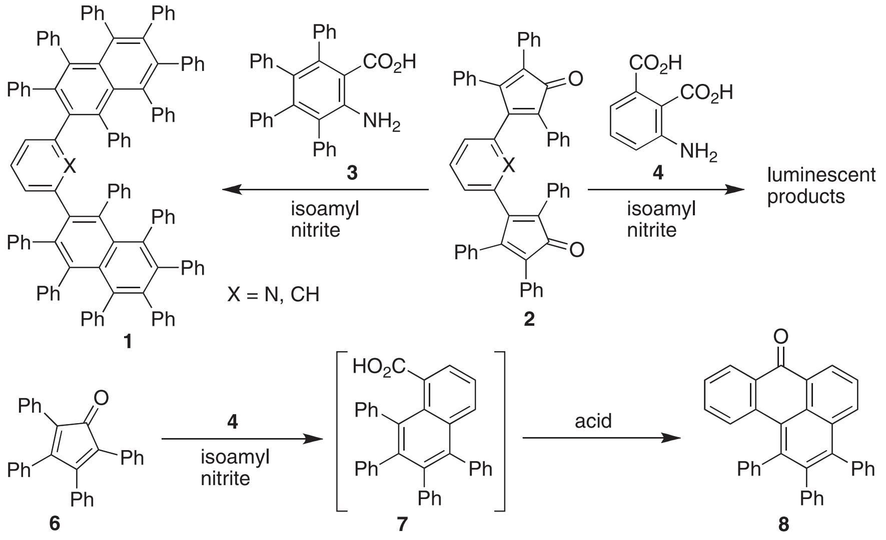
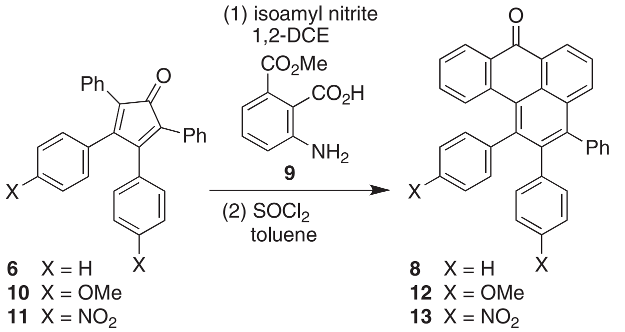
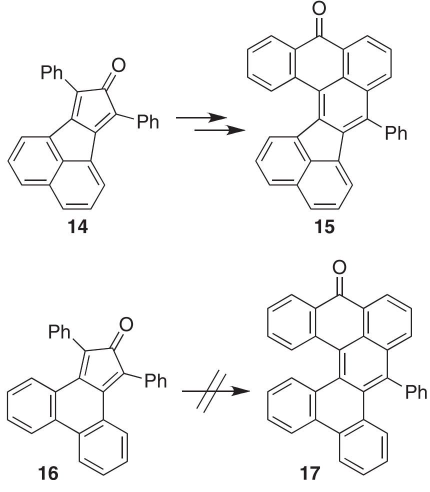


Scheme 1.



Scheme 2.

Polyaryl cyclopentadienones with many different aryl substituents are known,[12] and provide a means to explore the effects of electron donors and acceptors on the emission of these new lumiphores. Both dimethoxy (**10**) and dinitro (**11**) tetracyclones[13,14] were employed as precursors in the synthesis to give the corresponding triarylmesobenzanthrones **12** and **13**. In addition, acecyclone[15] (**14**, Scheme 3) and phencyclone[16,17] (**16**)—cyclopentadienones with larger polycyclic aromatic cores—were also utilized in the mesobenzanthrone synthesis. Acecyclone was readily converted to the extremely luminescent, yellow compound **15**. However, the reaction with phencyclone gave a product with a bright orange luminescence, presumably compound **17**, but in several trials this material was never isolated in pure form.



Scheme 3.

Mesobenzanthrones **8**, **12**, **13**, and **15** are all yellow crystalline solids, but compound **12** gave particularly nice needles from alcohol solutions, and its X-ray structure was determined. The molecular structure of one of the two crystallographically independent molecules of **12** is illustrated in Fig. 1. Notably, the anthrone core is slightly twisted[18] in these molecules due to the crowding of the aryl groups. Thus, the torsion angles C(4)–C(5)–C(11)–C(12) (crystallographic numbering) are 8.5° and 12.3° for the two independent molecules. In addition, the various phenyl rings are twisted with respect to the mesobenzanthrone core by 66° to 85°, but in spite of the presumably poor conjugation of their methoxy substituents with the core, as well as that of the nitro substituents in **13**, these groups proved to have very significant effects on the luminescence.

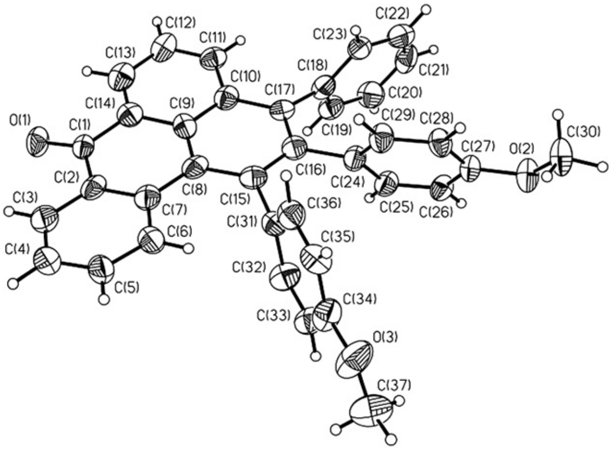


Fig. 1. Molecular structure of compound **12**. Thermal ellipsoids are plotted at the 50% probability level.

2.2. Photochemical behavior

The spectrophotometric and luminescence data for the series of mesobenzanthones are given in Table 1. All of the compounds absorb in the blue and luminesce in the green/yellow with widely varying efficiencies. Fig. 2 shows the absorption and fluorescence spectra for the series in both methanol and acetonitrile. Compounds

Table 1
Spectrophotometric and luminescence data for compounds **8**, **12**, **13**, and **15**

Compounds	**8**		**12**		**13**		**15**	
Solvent	MeOH	MeCN	MeOH	MeCN	MeOH	MeCN	MeOH	MeCN
Absorbance max (nm)	407	401	407	402	400	396	461	462
Emission max (nm)	521	498	579	527	509	496	562	519
Stokes shift (μm^{-1})	5400	4900	7300	5900	5400	5100	3900	2400
Quantum yield	1.0	0.04	0.05	0.55	0.06	0.01	0.97	0.91
Lifetime (ns)	9.2	0.6	0.8	2.3	0.6	< 0.3	9.4	6.6
ε (M^{-1} cm^{-1})	1.2×10^4	1.6×10^4	3.6×10^3	2.5×10^3	6.9×10^3	1.1×10^4	6.0×10^3	8.9×10^3
k_r (s^{-1})	1.1×10^8	6×10^7	6×10^7	2.4×10^8	1.0×10^8		1.0×10^8	1.4×10^8
k_{nr} (s^{-1})	0	1.5×10^9	1.2×10^9	2.0×10^8	1.6×10^9		3×10^6	1×10^7

8, **12**, and **13** have broad, featureless UV spectra with maxima close to 400 nm. The absorption of the fused aryl derivative **15** is significantly red shifted (λ_{max} ~460 nm) relative to the others, and it exhibits some vibronic structure, especially in acetonitrile. For all the derivatives, only small differences exist between the absorption maxima in methanol and acetonitrile. In contrast, the fluorescence of all the derivatives shifts to the red upon changing the solvent from acetonitrile to methanol. The magnitude of the solvent shift varies with structure and is largest for the dimethoxy (**12**) and fused aryl (**15**) derivatives. The spectra in Fig. 2 are normalized to illustrate these differences in the fluorescence maxima.

The dinitro derivative (**13**) is only weakly luminescent in both solvents. The parent compound (**8**) and its dimethoxy derivative (**12**) exhibit large differences in emission intensity with solvent, and **15** exhibits intense luminescence in both solvents studied. Radiative decay rate constants were obtained from emission quantum yield and lifetime data in both methanol and acetonitrile for all the derivatives. The values obtained vary by only a factor of four for all the substances; however, nonradiative relaxation rate constants span nearly three orders of magnitude.

The photophysical behavior of the triphenyl compound **8** generally parallels that of simpler mesobenzanthrones. A thorough investigation of monosubstituted mesobenzanthrones was reported in a series of papers by McKellar and colleagues.[4–6] This work examined anilino, amino, hydroxyl, and methoxy derivatives in the 3-, 4-, 6-, and 8-positions. The effects of solvent polarity on the absorption spectra, emission spectra, and quantum yield of the various analogs were reported. The long wavelength absorption shifts to the red as solvent polarity increases, and absorption maxima range from 400 to 500 nm with a typical solvent shift (ether–methanol) of 20 nm. The fluorescence maxima also shift to the red as the solvent polarity increases, with the most dramatic shift in the 3-methoxy derivative with fluorescence maxima of 473 nm in hexane and 544 nm in methanol, respectively. The fluorescence quantum yields varied greatly across the series, generally increasing with the solvent polarity; thus the 3-methoxy derivative has a quantum yield of 0.02 in hexane and 0.76 in methanol. Comparable effects are observed for compound **8**, upon shifting from the less polar acetonitrile to the more polar methanol, on the absorption maxima (401 to 407 nm), emission maxima (498 to 521 nm), and quantum yield (0.04 to 1) (see Table 1).

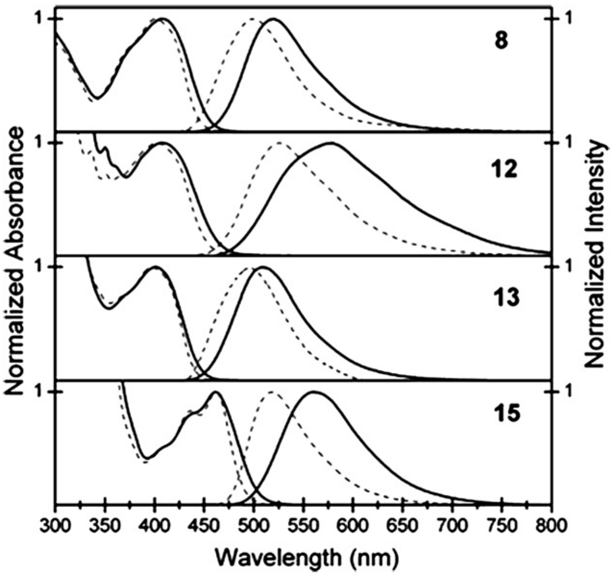


Fig. 2. Absorption and luminescence spectra of compounds **8**, **12**, **13**, and **15** in methanol (solid line) and acetonitrile (dashed line). Spectra are normalized for presentation purposes; molar absorptivities and emission quantum yields are reported in Table 1.

In contrast, the addition of two methoxy groups or two nitro groups to peripheral phenyls of compound **8** (to form **12** and **13**, respectively) dramatically changes the emissive behavior of the system, and in quite different ways for the two derivatives. Briefly stated, the solvent shift on the emission maxima for dimethoxy compound **12** is substantially larger than for **8** (though in the same direction for both), but the quantum yield for **12** is far higher in the less polar acetonitrile (0.55) than in the more polar methanol (0.05), a surprising inversion of the result observed for **8**. For the dinitro compound **13**, the emission in very weak in both solvents and the spectral shifts are the smallest of all the substances reported here.

In order to explain these differences, produced by substituents on phenyl rings that are essentially out of conjugation with the main chromophore, DFT and time-dependent DFT (TDDFT) calculations were carried out for all compounds at the B3PW91/6-31G(d) level of theory. Geometry-optimized singlet ground state structures were employed as input for TDDFT calculations to determine several of the lowest energy singlet and triplet electronic transitions for each compound, both in the gas phase and with the inclusion of acetonitrile or methanol solvent by means of a polarized continuum model (see the Experimental section for additional details). From these calculations it is clear that the nature of the lowest allowed transition in each molecule is quite different from those in the others.

The triphenyl compound **8** has photophysical behavior that parallels that of the mesobenzanthrone derivatives reported by McKellar et al. For this molecule the HOMO and LUMO of the ground state are both largely localized on the benzanthrone ring system (see the Supplementary data), and the lowest energy allowed transition is of π–π^* character and dominated by the HOMO to LUMO transition.

In contrast, for compound **12**, the HOMO is localized on the two methoxyphenyl groups while the LUMO is a π^* orbital of the benzanthrone (see the Supplementary data). The lowest energy transition clearly involves charge transfer from the methoxyphenyls to the benzanthrone ring system, and this is reflected in the large difference in emission maxima in acetonitrile and methanol. The seeming anomaly that the quantum yield for **12** is lower in methanol than acetonitrile is easily explained by another DFT result: the energy gap between the excited singlet state and the triplet state is significantly lower in methanol than in acetonitrile. This observation is unique to compound **12** among the chromophores studied, and provides an explanation for the solvent dependence of the emission quantum yields in that the smaller singlet-triplet gap should result in more efficient population of the triplet state.[19]

For compound **13**, the nitro analog, the TDDFT results indicate the lowest energy allowed transition involves charge transfer from the benzanthrone ring *to* a nitrophenyl group (see the Supplementary data), just the opposite of the situation in **12**. Thus this chromophore is yet different from the others.

And what of the intensely fluorescent, fused-ring polycycle **15**? The structured absorption spectrum of compound **15**, along with the smaller Stokes shift and the very high emission yield in a relatively nonpolar solvent, suggests that its photophysical behavior more nearly parallels that of benzo[*k*]fluoranthene,[20] a substructure of **15**′s ring system, rather than that of the mesobenzanthrones. The TDDFT analysis for **15** indicates that the lowest energy allowed transition is the HOMO–LUMO transition possessing $\pi-\pi^*$ character. However, while the HOMO closely resembles the HOMO of benzo[*k*]fluoranthene, the LUMO has a greater orbital contribution on the benzanthrone portion of the molecule. The strong solvent dependence of the emission maximum suggests some degree of charge transfer for the transition, and this is reflected in the differential orbital occupancies of the HOMO and LUMO.

3. Conclusion

The four compounds described above are just a tiny fraction of similar lumiphores that might be prepared by using the general, one-pot synthesis of polyaryl mesobenzanthrones from tetraarylcyclopentadienones. The particular examples studied all absorb in the blue and emit strongly in the green/yellow region of the spectrum, but inclusion of different aryl groups will no doubt increase the range of colors. Variation of the aryl substituents not only can modify the photophysical properties of these compounds, but also can provide convenient points of attachment of the chromophores to other substrates. In sum, the polyaryl mesobenzanthrones are a promising new class of organic lumiphores.

4. Experimental

4.1. General information

2-Amino-6-(methoxycarbonyl)benzoic acid (**9**) was prepared by the method of Rogers and Averill.[11] However, the material was of inconsistent purity (the authors note that **9** is unstable at room temperature), and it was always used in large excess. 3,4-Bis(4-methoxyphenyl)-2,5-diphenylcyclopentadienone[13] (**10**), 3,4-bis(4-nitrophenyl)-2,5-diphenylcyclopentadienone[14] (**11**), and acecyclone[15] (**14**) were prepared as described previously. All other solvents and reagents were commercial, reagent grade materials, and they were used without further purification. ^{1}H NMR spectra were recorded at 400 MHz on a Varian Unity INOVA spectrometer; samples were dissolved in $CDCl_3$. ^{13}C NMR spectra were recorded on the same instrument at 101 MHz. High-resolution ESI-TOF and EI mass spectra were recorded on Agilent 6220 and Kratos MS-50 RFA spectrometers, respectively.

4.2. Data for compounds

*4.2.1. 1,2,3-Triphenyl-7H-benz[de]anthracen-7-one (1,2,3-triphenylmesobenzanthrone) (**8**).* A solution of tetraphenylcyclopentadienone (**6**, 0.200 g, 0.520 mmol) in 1,2-dichloroethane (DCE, 20 mL) was heated to a gentle reflux. A solution of isoamyl nitrite (0.50 mL, 3.7 mmol) in DCE (10 mL) was added, and the heating continued for 10 min. A suspension of 2-amino-6-(methoxycarbonyl)benzoic acid (**9**, 0.505 g, nominally 2.60 mmol) in DCE (30 mL) was then added in 10 equal portions, and the resulting mixture was heated at reflux for 2 h. A 2 M NaOH solution (5 mL) was added to quench the reaction, and it was cooled to room temperature. The reaction mixture was then poured into 3 M HCl (100 mL) and it was extracted with $CHCl_3$ (50 mL). The organic layer was dried over Na_2SO_4, and then the solvent was stripped off. The remaining material was dissolved in toluene (100 mL), $SOCl_2$ (2 mL) was added, and the solution was heated at reflux for 16 h. After removal of solvent, the residue was chromatographed on silica gel (solvent, 2:1 hexanes–CH_2Cl_2, followed by CH_2Cl_2) to give a yellow solid (104 mg). Recrystallization of this material from $CHCl_3$–MeOH yielded compound **8** (97.0 mg, 0.212 mmol, 40.8%). A portion of this material (23.1 mg, 0.0504 mmol) was further purified by preparative TLC (R_f 0.52; solvent, toluene) and recrystallization from ethanol to give **8** of high purity (20.1 mg, 0.0438 mmol). ^{1}H NMR ($CDCl_3$) δ 6.75 (m, 2H), 6.90 (m, 3H), 7.07–7.25 (m, 12H), 7.34 (ddd, J=8.0, 6.5, 1.5 Hz, 1H), 7.68 (dd, J=8.5, 7.5 Hz, 1H), 7.94 (dd, J=8.5, 1.5 Hz, 1H), 8.46 (ddd, J=8.0, 1.0, 1.0 Hz, 1H), 8.80 (dd, J=7.5, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 125.2, 125.6, 126.3, 126.7, 126.9, 127.0, 127.3, 127.5, 127.6, 128.3, 128.4, 128.6, 129.6, 130.1, 131.0, 131.1, 131.2, 131.6, 131.9, 132.8, 134.3, 137.4, 138.8, 139.5, 141.1, 141.7, 141.9, 184.4 (28 of 29 expected resonances observed); HRMS (ESI) m/z 459.1746 (M+H), calcd for $C_{35}H_{23}O$ 459.1749.

*4.2.2. 1,2-Bis(4-methoxyphenyl)-3-phenyl-7H-benz[de]anthracen-7-one (**12**).* 3,4-Bis(4-methoxyphenyl)-2,5-diphenylcyclopentadienone (**10**, 0.201 g, 0.452 mmol) was subjected to the aryne addition and cyclization described for the preparation of **8**. The crude, concentrated reaction mixture was chromatographed on silica gel (solvent, 7:5 hexanes–CH_2Cl_2, followed by 1:1 hexanes–CH_2Cl_2) to give a yellow solid (35.8 mg). Recrystallization of this material from $CHCl_3$–MeOH yielded compound **12** of approximately 90% purity (27.2 mg, 0.0524 mmol, 11.6%). A portion of the product (19.9 mg, 0.0384 mmol) was further purified by preparative TLC (R_f 0.34; solvent, toluene) and recrystallization from ethanol to give **12** (19.2 mg, 0.0370 mmol); ^{1}H NMR ($CDCl_3$) δ 3.67 (s, 3H), 3.78 (s, 3H), 6.47 and 6.64 (AA′BB′ system, 4H), 6.71and 6.93 (AA′BB′ system, 4H), 7.11–7.26 (m, 10H), 7.34 (ddd, J=8, 5, 3 Hz, 1H), 7.64 (dd, J=8.5, 7.5 Hz, 1H), 7.89 (dd, J=8.5, 1.5 Hz, 1H), 8.45 (d, J=7.5 Hz, 1H), 8.76 (dd, J=6, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.0, 55.2, 112.3, 113.8, 125.3, 126.1, 126.7, 127.1, 127.4, 127.6, 128.4, 128.6, 129.4, 130.1, 130.9, 131.6, 131.9, 132.2, 132.3, 132.8, 134.1, 134.2, 137.7, 139.0, 141.0, 141.4, 141.8, 157.3, 158.6, 184.5 (30 of 30 expected resonances observed); HRMS (ESI) m/z 519.1950 (M+H), calcd for $C_{37}H_{27}O_3$ 519.1960.

*4.2.3. 1,2-Bis(4-nitrophenyl)-3-phenyl-7H-benz[de]anthracen-7-one (**13**).* 3,4-Bis(4-nitrophenyl)-2,5-diphenylcyclopentadienone (**11**, 0.200 g, 0.422 mmol) was subjected to the aryne addition and cyclization described for the preparation of **8**. The crude, concentrated reaction mixture was chromatographed on silica gel (solvent, 2:1 hexanes–CH_2Cl_2, followed by 1:1 hexanes–CH_2Cl_2) to give a yellow solid (104 mg; R_f 0.30 upon TLC; solvent, toluene). Recrystallization from ethanol yielded pure compound **13** (81.3 mg, 0.148 mmol, 35.1%); ^{1}H NMR ($CDCl_3$) δ 6.95 and 7.83 (AA′BB′ system, 4H), 7.10 (m, 2H), 7.16 (ddd, J=8.5, 7.0, 1.5 Hz, 1H), 7.26–7.29 (m, 4H), 7.31 and 8.08 (AA′BB′ system, 4H), 7.42 (t, J=7.5 Hz, 1H), 7.75 (dd, J=8.5, 7.5 Hz, 1H), 7.94 (dd, J=8.5, 1.5 Hz, 1H), 8.50 (dd, J=8.0, 1.5 Hz, 1H), 8.83 (dd, J=7.0, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 122.4, 123.9, 126.2, 127.4, 127.8, 128.2, 128.3, 128.9, 129.8, 130.6, 131.4, 132.0, 132.1, 133.0, 133.9, 134.3, 135.3, 135.8, 136.0, 137.3, 137.5, 137.8, 146.0, 146.4, 146.9, 148.4, 183.8 (27 of 29 expected resonances observed); HRMS (ESI) m/z 549.1447 (M+H), calcd for $C_{35}H_{21}N_2O_5$ 549.1450.

*4.2.4. 9-Phenyl-5H-anthro[9,1-jk]fluoranthen-5-one (**15**).* Acecyclone (**14**, 0.100 g, 0.281 mmol) was subjected to the aryne addition and cyclization described for the preparation of **8**. The crude, concentrated reaction mixture was chromatographed on silica gel (solvent, 2:1 hexanes–CH_2Cl_2) to give a yellow solid (22.8 mg). Recrystallization of this material from $CHCl_3$–MeOH yielded compound **15** (21.0 mg, 0.0488 mmol, 17.3%). A portion of the product (20.0 mg, 0.0465 mmol) was further purified by preparative TLC (R_f 0.45; solvent, toluene) and recrystallization from ethanol to give **15** of high purity (17.5 mg, 0.0407 mmol); ^{1}H NMR ($CDCl_3$) δ 6.57 (d, J=7.0 Hz, 1H), 7.36 (dd, J=8.0, 7.0 Hz, 1H), 7.53 (m, 2H), 7.61–7.69 (m, 7H), 7.80 (d, J=8.0 Hz, 1H), 7.90 (d, J=7.0 Hz, 1H), 7.92 (dd, J=8.0, 2.0 Hz, 1H), 8.52 (dd, J=8.0, 1.5 Hz, 1H), 8.66 (dd, J=7.5, 1.5 Hz, 1H), 8.74 (d, J=7.5 Hz, 1H), 9.19 (d, J=7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 122.8, 123.8, 124.9, 126.2, 126.6, 127.4, 127.7, 127.9, 128.0, 128.3, 128.4, 128.8, 128.9, 129.0, 129.3, 129.9, 130.4, 131.8, 132.2, 132.4, 133.0, 135.6, 135.8, 136.4, 136.5, 136.6, 137.3, 137.4, 137.8, 184.4 (30 of 29 expected resonances observed); HRMS (EI) m/z 430.1356 (M^+), calcd for $C_{33}H_{19}O$ 430.1358.

4.3. Photochemical studies

All electronic absorption spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer. All fluorescence spectra were obtained by using an SPEX Fluorolog spectrofluorimeter equipped with a 450-W Xe arc lamp, single grating monochromators with fixed slits, and a thermoelectrically cooled ANDOR CCD detector. Luminescence quantum yields were determined from the integrated corrected emission spectra of the mesobenzanthrone derivatives relative to anthracene as a reference. The mesobenzanthrones were absorbance matched to the anthracene standard at 394 nm and then degassed with nitrogen for 10 min prior to the measurement of the emission spectra. Luminescence lifetimes were obtained by the time-correlated single photon counting technique. Each sample was excited using an IBH NanoLED pulsed diode laser source at either 377 or 440 nm. The emitted light was collected at right angles to the excitation pulse, filtered through bandpass filters (Andover Corporation) and collected by an IBH Model TBX-04 cooled photomultiplier (PMT) detector. The output of the PMT served as the input for the stop channel of the time to amplitude converter (TAC, Tennelec TC-863). Start pulses for the TAC were obtained from the synchronous TTL output of the NanoLED laser source. The output from the TAC was directed to a multichannel analyzer (Ortec, Easy MCA), where the signal was accumulated. Laser light scattered from a non-luminescent solution was used to accumulate instrument response profiles. The data were analyzed as single or double exponential decays using a deconvolution routine developed by PTI Instruments.

4.4. Computational studies

All hybrid density functional calculations were performed at the B3PW91/6-31G(d) level[21–23] using Gaussian 03 or Gaussian 09,[24,25] and the built-in default thresholds for wave function and gradient convergence were employed. Full geometry optimizations were performed with both singlet and triplet wavefunctions for all molecules. The optimized singlet geometries were used as the input for TDDFT calculations at the same level of theory. These calculations were used to determine several (typically 10 each) of the lowest energy singlet and triplet electronic transitions for each compound, both in the gas phase and with the inclusion of acetonitrile or methanol solvent by means of a polarized continuum model. Solvent inclusion significantly changes the location of charge density when compared to the results of gas phase calculations, but negligible differences exist between the orbitals obtained in the two solvents.

Acknowledgements

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Supplementary data

(1) A PDF file containing ^{1}H and ^{13}C NMR spectra of compounds **8**, **12**, **13**, and **15**, images of the calculated HOMO and LUMO for **8**, **12**, **13**, and **15**, and full Refs. 24,25 and (2) an ASCII text file containing the atomic coordinates and energies of the calculated structures of **8**, **12**, **13**, and **15**. Crystallographic data (excluding structure factors) for the structure of **12** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 823793. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.07.018.

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