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Perylen-3-ylmethyl: fluorescent photoremovable protecting group (FPRPG) for carboxylic acids and alcohols

Avijit Jana, Mohammed Ikbal, N.D. Pradeep Singh *

Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

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ABSTRACT

Perylen-3-ylmethyl demonstrated as a new fluorescent photoremovable protecting group (FPRPG) for carboxylic acids and alcohols. Carboxylic acids including amino acids were protected as their corresponding esters by coupling with FPRPG, perylen-3-ylmethyl. Photophysical studies of caged esters showed that they all exhibited strong fluorescence properties and their fluorescence quantum yields were in the range of 0.85–0.95. Irradiation of the caged esters using visible light (≥410 nm) in aqueous acetonitrile released the corresponding carboxylic acids in high chemical (94–97%) and quantum (0.072–0.093) yields. The results obtained from the photolysis of the caged ester in different solvents indicated that solvent has influence on the rate of photorelease. Further, we also explored the ability of FPRPG, perylen-3-ylmethyl for the protection of alcohols and phenols.

1. Introduction

Photoremovable protecting groups (PRPGs) with fluorescent properties have thrown light in the study of numerous processes in biology[1–3] and medicine.[4,5] Fluorescent PRPGs (FPRPGs) have certain advantages over PRPGs, since they not only release active molecules of interest at desired location for a specific period of time, but also allow us to visualize, quantify, and follow the spatial distribution, localization, and depletion of the active molecules by monitoring its fluorescent caged precursors using fluorescent microscope techniques.[6]

Although FPRPGs are of great utility, attempts to synthesize either FPRPGs or to modify a PRPG into fluorescence photolabile group are limited. Initially, Burgess et al.[7] reported fluorophore based on dansyl derivative, which on irradiation using UV light (365 nm) resulted in deprotection of carboxylic acids, rather with low photolysis efficiency and chemical yield. Based on the above strategy, polycyclic aromatic compounds, which are fluorophores namely anthraquinone,[8] pyrene,[8,9] phenanthrene,[8] anthracene,[10] and coumarins[11] moieties have been targeted as FPRPGs.

So far, 7-methoxycoumarin-4-yl,[11,12] anthracene-9-methanol,[10] and pyren-1-ylmethyl[8–10,13–15] were demonstrated as FPRPGs for various functional groups. However, the above-mentioned FPRPGs have certain limitations like moderate quantum yields, needs specific solvent for the photoreaction, and no stronger absorption band ≥410 nm. Based on the above facts and together with our recent research interest on FPRPGs,[16] herein, we report a new FPRPG namely perylen-3-ylmethyl (**1**), with improved photophysical and photochemical properties for carboxylic acids and alcohols.

2. Results and discussion

2.1. Synthesis of caged esters (4a–h)

A series of carboxylic acids including amino acids were protected by 3-(bromomethyl)perylene (**2**) in the form of caged esters (**4a–h**) as outlined in Schemes 1 and 2 were readily prepared from 3-(hydroxymethyl)perylene (**1**) by reaction with phosphorus tribromide (PBr_3) in carbon tetrachloride (CCl_4). Treatment of carboxylic acids (**3a–c**) with 1 equiv of **2** in the presence of K_2CO_3/KI in dry *N*,*N*-dimethylformamide (DMF) at room temperature for a period of 8–12 h afforded the caged esters in excellent yields (Table 1, **4a–c**). While, for the protection of amino acids we used corresponding Boc-protected amino acids (**3d–h**), and they were protected similar to carboxylic acids in good yields (Table 1, **4d–h**), except KF was used in place of KI. All the caged esters (**4a–h**) were characterized by IR, ^1H, ^{13}C NMR, and mass spectral analysis.

2.2. Photophysical properties of caged esters (4a–h)

UV/vis absorption and emission spectra of degassed 2×10^{-6} M solution of caged esters (**4a–h**) and 3-(hydroxymethyl)perylene (**1**)

* Corresponding author. Tel.: +91 3222 282324; fax: +91 3222 282252; e-mail address: ndpradeep@chem.iitkgp.ernet.in (N.D.P. Singh).

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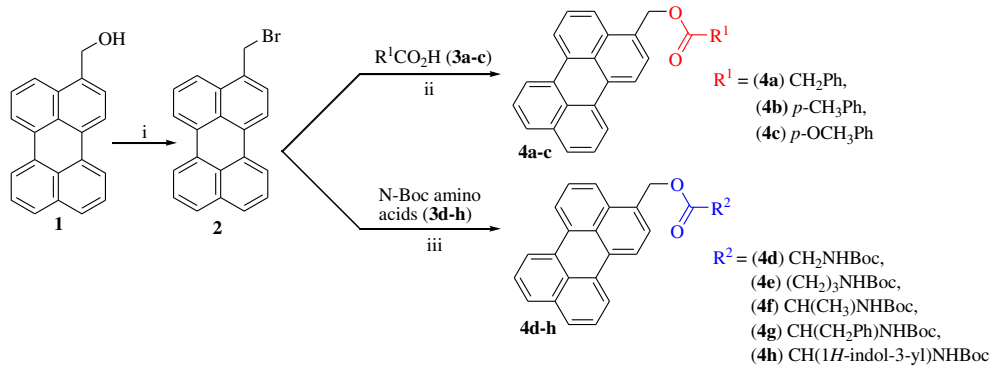


Reagents: i, PBr_3/CCl_4, 80 °C, 4 h; ii, K_2CO_3/KI/DMF, rt, 8-12 h; iii, K_2CO_3/KF/DMF, rt, 8-12 h;

Scheme 1. Synthesis of caged esters (**4a**–**h**) of perylen-3-ylmethyl.

Table 1
Synthetic yields of the caged esters (**4a**–**h**), UV/vis absorption and fluorescence data of caged esters (**4a**–**h**) and its precursor 3-(hydroxymethyl)perylene (**1**) in absolute ethanol

Caged ester	Synthetic yield[a] (%)	UV/vis absorption		Fluorescence	
		λ_{max}[b] (nm)	log ε[c]	λ_{max}[d] (nm)	Φ_f[e]
4a	91	438	4.38	445	0.92
4b	88	438	4.39	445	0.93
4c	86	439	4.55	447	0.93
4d	80	439	4.40	446	0.87
4e	76	439	4.39	446	0.87
4f	75	437	4.39	443	0.88
4g	79	440	4.40	447	0.86
4h	82	435	4.40	447	0.86
1	–	439	4.55	446	0.95

[a] Based on isolated yield.
[b] Maximum absorption wavelength.
[c] Molar absorption coefficient at the maximum absorption wavelength.
[d] Maximum emission wavelength.
[e] Fluorescence quantum yield (excitation wavelength 390 nm, error limit within ±5%).

in absolute ethanol (EtOH) were recorded. The absorption and emission maxima, molar absorptivities, and fluorescence quantum yield of the above esters along with **1** are summarized in Table 1. Fluorescence quantum yield was calculated using 9,10-diphenylanthracene as standard (Φ_f=0.95 in ethanol).[17]

Fig. 1 shows the normalized absorption and the emission spectra of caged ester **4c** in ethanol. The absorption spectrum of **4c** showed three strong absorption bands centered at 390, 410, and 439 nm (π–π^* transition), and its emission spectrum found to be a mirror image of its absorption spectrum with three emission bands at 445, 480, and 510 nm (Fig. 1), typical characteristics of the perylene moiety.[18]

We observed similar absorption and emission behavior for all other caged esters (Fig. 2 a and b).

Further, the fluorescence quantum yields, Φ_f, for caged esters (**4a**–**h**) in absolute ethanol (EtOH) at room temperature were in the range of 0.86–0.93 (Table 1), indicates that caged esters are highly fluorescent. Moreover, the photophysical properties of caged esters were found to be similar to FPRPG (**1**), which suggested that perylene moiety only dictates the absorption and emission maxima of caged esters ruling out the influence of its counterpart carboxylic acids.

2.3. Photolysis of caged esters (4a–h)

Considering our main interest to study the application of perylene-3-ylmethyl as an FPRPG, we irradiated caged esters (**4a**–**h**) (1.0×10^{-4} M) individually in acetonitrile/H_2O (75/25 v/v) using 125 W medium pressure Hg lamp as visible light source ($\geq$410 nm) and 1 M $NaNO_2$ solution as UV cut-off filter. We found for all the

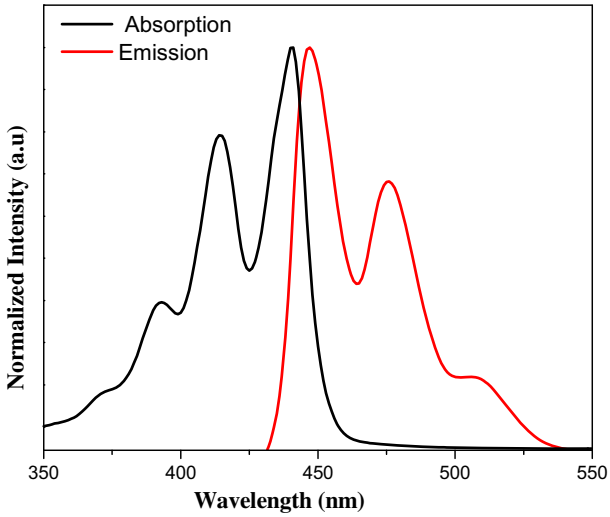


Fig. 1. Normalized UV/vis absorption spectrum (black line) and emission spectrum (red line) of caged ester **4c** in EtOH.

caged esters their corresponding carboxylic acids (**3a**–**h**) were released in high chemical (94–97%) and quantum (0.072–0.093) yields (Φ_p) (Table 2).

For all caged esters mentioned in Table 2, the photoproducts were isolated and analyzed by spectroscopy and in every case we found the released carboxylic acid was the only significant photoproduct in addition to the FPRPG (**1**). The quantum yield (Φ_p) was calculated using potassium ferrioxalate as an actinometer.[19,20]

As a representative example, we have shown in Fig. 3 the HPLC profile of caged ester **4c** at regular intervals of irradiation. The HPLC chart shows gradual depletion of the peak at t_R 6.77 min with an increase in irradiation time, indicating the photodecomposition of the caged ester **4c**. On the other hand, we also noted a gradual increase of two new major peaks at t_R 4.25 min and t_R 2.20 min, corresponding to the photoproducts 3-(hydroxymethyl)perylene (**1**) and 4-methoxybenzoic acid (**3c**), respectively.

Further, we also monitored the course of photorelease of caged ester **4c** using UV/vis and fluorescence spectroscopy (Supplementary data Figs. S.1.a and S.1.b).

2.4. The effect of solvent on photorelease

To understand the solvent effect on the rate of photorelease of carboxylic acids, we irradiated caged ester **4c** in different solvents

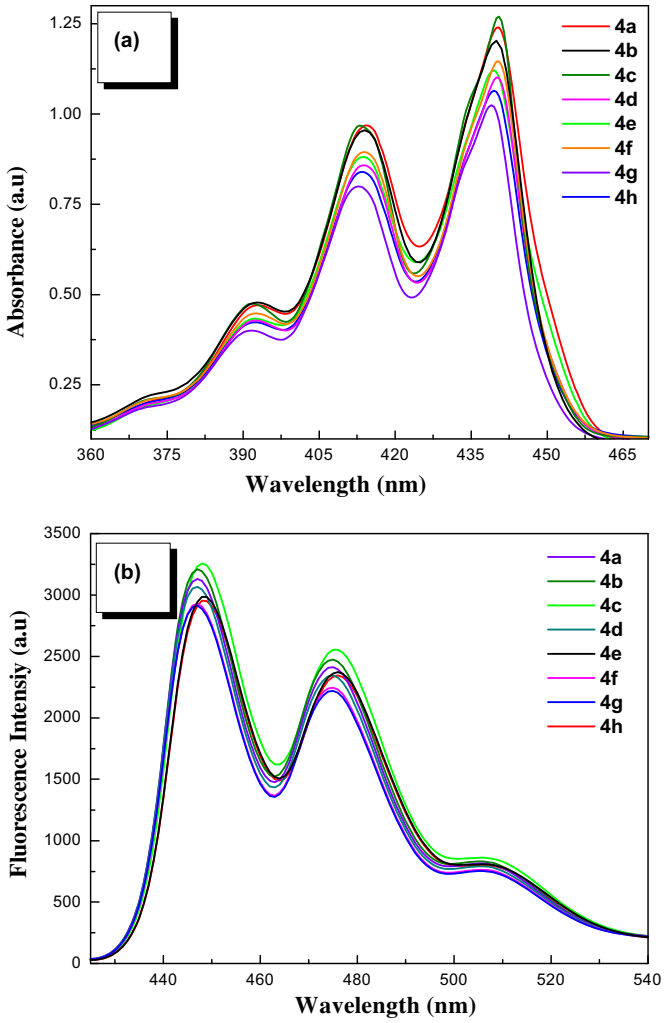


Fig. 2. (a) UV/vis absorption spectra of caged esters (**4a**–**h**). (b) Fluorescence spectra of caged esters (**4a**–**h**).

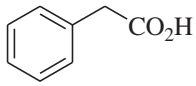
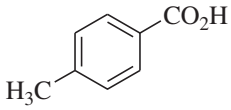
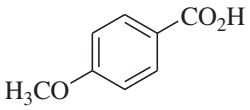
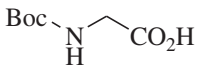
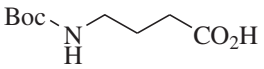
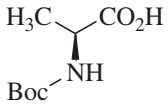
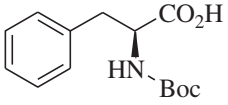
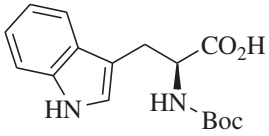
and the results are summarised in Table 3. We noticed caged ester **4c** released 4-methoxybenzoic acid more efficiently in methanol/H_2O (95/5) compared to acetonitrile/H_2O (95/5) and dioxane/H_2O (75/25). The above fact can be attributed due to the formation of ionic intermediates during photolysis (Scheme 2) and on the nature of the solvent (since hydrogen bonding and the polarity of the solvent have an influence on the excited states). Though the photocleavage of caged esters in methanol is efficient their solubility in methanol is not as good as compared to acetonitrile.

Further, we also noticed the efficiency of the photorelease of caged ester **4c** increases continuously with increasing the amount of water (quantum yield for the release of 4-methoxybenzoic acid by caged ester **4c** increased by ~30 times as we move from 5% to 25% of water in acetonitrile). The interpretation for the increase of quantum yield is due to the better stabilization of the newly generated ion pair (Scheme 2) by solvation, the similar phenomenon was also noted in the case of caged coumarins.[11]

2.5. Mechanism of photorelease

Literature precedence[10,11,16] and the above solvent study suggest that the photolysis of caged esters proceeds through an ionic mechanism. The initial photochemical step involves excitation of the perylene-3-ylmethyl chromophore to its singlet excited state, which then undergoes heterolysis of the C–O ester bond (photo-S_N1) to produce an ion pair of perylene-3-ylmethyl carbocation and

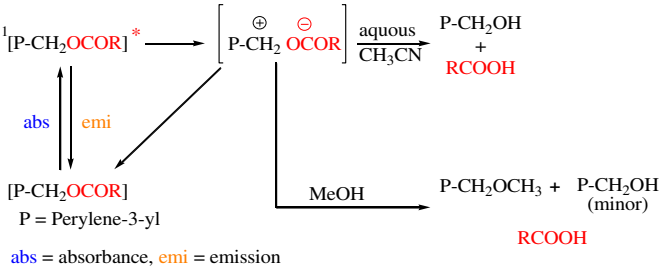
Table 2
Photolytic data of caged esters (**4a**–**h**) on irradiation by visible light (≥410 nm) in acetonitrile/H_2O (75/25) solution

Ester	Photolytic data of caged esters (**4a**–**h**)			
	Acid	% of ester depleted[a]	% of acid released[b]	Quantum yield[c] (Φ_p)
4a		98	96	0.090
4b		97	96	0.091
4c		98	97	0.093
4d		95	95	0.089
4e		95	94	0.072
4f		98	97	0.087
4g		95	94	0.087
4h		96	95	0.077

[a] % of caged ester depleted as determined by HPLC.
[b] % of carboxylic acid released as determined by HPLC.
[c] Photochemical quantum yield for the release of carboxylic acids (error limit within ±5%).

carboxylate anion. After ion-pair separation in a polar solvent, the methylenic carbocation and carboxylate anion reacts with solvent molecules to yield 3-(hydroxymethyl) perylene (**1**) and carboxylic acid, respectively (Scheme 2).

To support the formation of perylene-3-ylmethyl carbocation intermediate, we carried out photolysis of caged ester **4c** in MeOH/H_2O (95/5 v/v) and analysed the course of photolysis by HPLC at



Scheme 2. Possible mechanism for the photorelease.

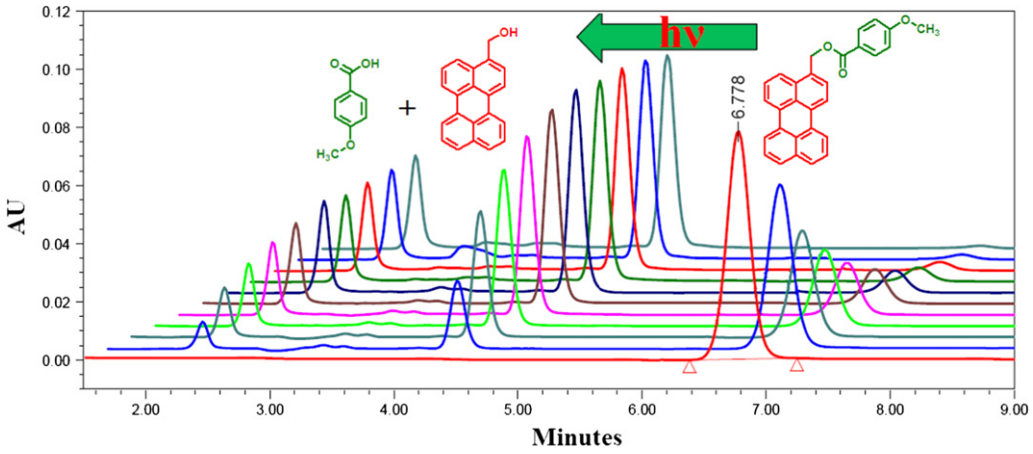


Fig. 3. HPLC profile of caged ester **4c** (1×10^{-4} M) in ACN/H_2O (75/25 v/v) at regular intervals of irradiation (0–50 min, time interval=5 min).

Table 3
Photolytic data of caged ester **4c** on irradiation by visible light (≥410 nm) in different solvents

Solvent	Photolytic data of caged ester **4c**		
	% of **4c** depleted[a]	% of **3c** released[b]	Quantum yield[c] (Φ_p)
CH_3CN	5	5	0.002
CH_3CN/H_2O (95/5)	11	10	0.004
CH_3CN/H_2O (90/10)	69	65	0.042
CH_3CN/H_2O (75/25)	98	97	0.093
Dioxane/H_2O (75/25)	82	75	0.062
CH_3OH	96	86	0.089
CH_3OH/H_2O (95/5)	98	89	0.093

[a] % of **4c** depleted as determined by HPLC.
[b] % of acid released as determined by HPLC.
[c] Photochemical quantum yield for the release of **4c** (error limit within ±5%).

regular intervals of irradiation. The HPLC chart (Fig. 4) showed the appearance of new peak at t_R 5.33 min in addition to peak at t_R 2.11 min, which correspond to 4-methoxybenzoic acid. The new peak at t_R 5.33 min was identified as 3-(methoxymethyl) perylene by isolating and analysing by spectroscopy. The formation of 3-(methoxymethyl) perylene suggests the trapping of perylene-3-ylmethyl carbocation by methanol.

Further to find out among two closely spacing strong absorption bands centered at 410 nm and 440 nm is responsible for the photocleavage of C–O bond, we irradiated ester conjugate **4c** (3 ml, ACN/H_2O, v/v 75/25) in a quartz cuvette at 410 nm and 440 nm UV light individually using fluorescence spectrophotometer with a 2.5 nm slit and the fluorescence spectra were recorded at regular interval of photolysis. The fluorescence spectra indicated photocleavage of **4c** was achieved on irradiation at 410 nm, while we noticed no change in emission spectra of **4c** on excitation at 440 nm (see Supplementary data, page no. S15), which suggest absorption band centered at 410 nm is responsible for photocleavage.

2.6. Synthesis of caged carbonates (7a–d)

To explore the versatility of our FPRPG (**1**), we carried out the protection of a series of alcohols including phenol as outlined in Scheme 3. Initially, we converted alcohols (**6a–d**) into their corresponding chloroformates by treating with triphosgene ($(COCl_2)_3$) at 0 °C. Treatment of alcohol chloroformates with FPRPG (**1**) in the presence of 4-dimethylaminopyridine (DMAP) in dry DCM resulted the corresponding caged carbonates (**7a–d**) in good yields (Table 4).

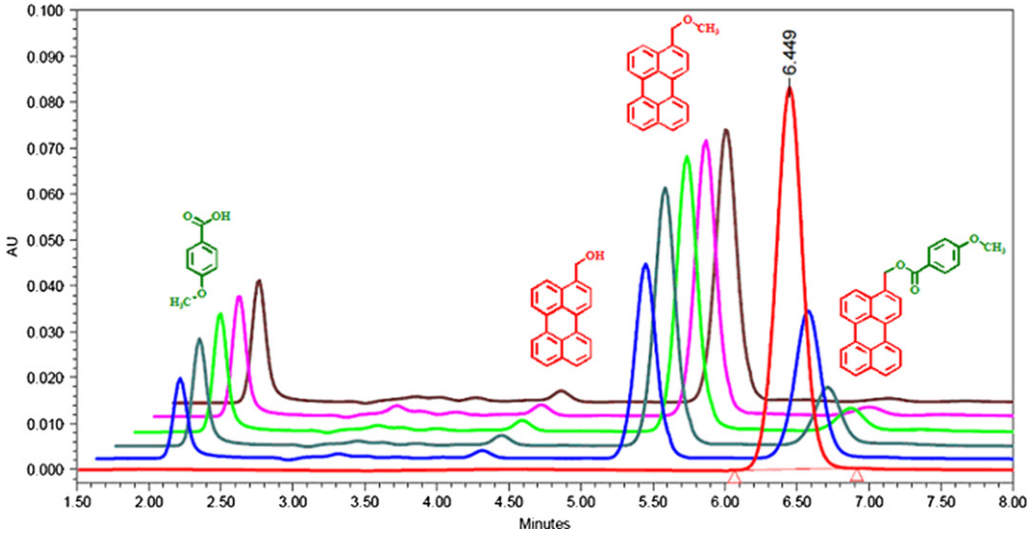
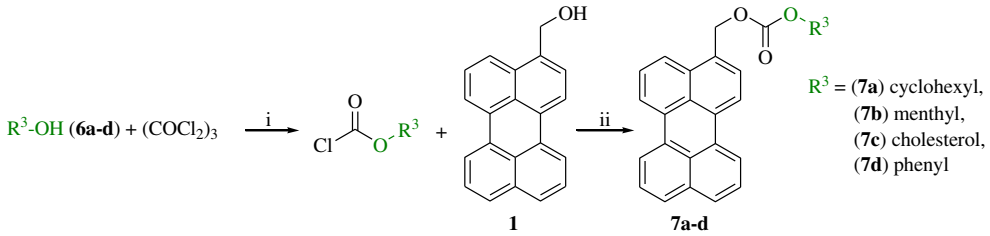


Fig. 4. HPLC profile of caged ester **4c** (1×10^{-4} M) in MeOH/H_2O (95/5 v/v) at regular intervals of irradiation (0–50 min, time interval=10 min).



Reagents: i, K_2CO_3, toluene, 0 °C, 4-5 h; ii, DMAP, DCM, rt, 8-12 h.

Scheme 3. Synthesis of caged carbonates (**7a**–**d**) of perylen-3-ylmethyl.

Table 4
Synthetic yields, UV/vis absorption, and fluorescence data of caged carbonates (**7a**–**d**) in absolute ethanol

Caged carbonate	Synthetic yield[a] (%)	UV/vis		Fluorescence	
		λ_{max}[b] (nm)	log ε[c]	λ_{max}[d] (nm)	Φ_f[e]
7a	76	440	4.39	447	0.92
7b	75	438	4.39	445	0.91
7c	79	440	4.40	447	0.91
7d	82	439	4.40	446	0.91

[a] Based on isolated yield.
[b] Maximum absorption wavelength.
[c] Molar absorption coefficient at the maximum absorption wavelength.
[d] Maximum emission wavelength.
[e] Fluorescence quantum yield (error limit within ±5%).

2.7. Photophysical properties of caged carbonates (7a–d)

The photophysical properties of caged carbonates (**7a**–**d**) were recorded as explained for caged esters and the results are summarized in Table 4. The absorption and emission maxima, molar absorptivities, and fluorescence quantum yield of carbonates were found to be analogous to caged esters, thus confirming the photophysical properties of caged compounds is dictated only by the perylene moiety (for absorption and emission spectra of carbonates (**7a**–**d**), see Supplementary data Figs. S.4.a and S.4.b).

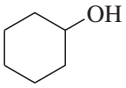
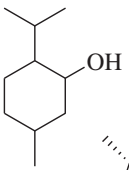
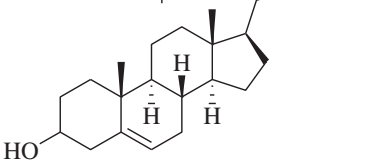
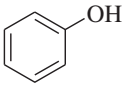
2.8. Photolysis of caged carbonates (7a–d)

Irradiation of carbonates (**7a**–**d**) using the procedure described for caged esters, resulted in the release of alcohols in quantitative yield (95–96%, Table 5). In each case, the photolysis was stopped when conversion reached at least 95% (as indicated by HPLC). For all caged compounds mentioned in Table 5, the photolysis products (corresponding alcohol and the protecting group **1**) were confirmed by isolating and matching their ^{1}H NMR spectra to those of authentic samples.

In similar to previously discussed caged esters, the mechanism of the photocleavage of carbonates involves heterolysis of the C–O ester bond to produce an ion pair of perylene-3-ylmethyl carbocation and carbonate anion. The newly generated carbonate anion undergoes decarboxylation[21,22] followed by proton abstraction from the solvent to produce alcohol.

The stability of caged compounds was performed by keeping the solution containing caged compound (**4a**–**c**, **e**, **h** and **7b**–**d**) individually in dark at three different initial pH values (4.5, 6, and 7.5) for a period of 30 days. We observed 7–15% decomposition for caged compounds by HPLC at three pH values (Supplementary data Table 1s).

Table 5
Photolytic data of carbonates (**7a**–**d**) on irradiation by visible light (≥410 nm) in acetonitrile/H_2O (75/25) solution

Carbonate	Photolytic data carbonates (**7a**–**d**)			
	Alcohol/Phenol	% of carbonate depleted[a]	% of alcohol released[b]	Quantum yield[c] (Φ_p)
7a		95	90	0.087
7b		96	91	0.086
7c		96	89	0.085
7d		95	90	0.088

[a] % of carbonate ester depleted as determined by HPLC.
[b] % of alcohol released as determined by ^{1}H NMR spectroscopy.
[c] Photochemical quantum yield for the release of alcohols (error limit within ±5%).

3. Conclusion

In summary, the newly developed FPRPG, perylene-3-ylmethyl exhibited unique properties like, good molar absorption coefficient in the visible wavelength region (≥410 nm) compared to anthracene-9-methanol and pyrene-1-ylmethyl, strong fluorescence and more important, releases carboxylic acids and alcohols with high chemical and quantum yield in aqueous condition by visible light. Though the present perylene chromophore can act as an efficient FPRPG still their water solubility needs to be improved. In future we will publish highly fluorescent and good water-soluble perylene chromophore having polar side chain on its bay area as an efficient FPRPG.

4. Experimental section

4.1. General

^{1}H NMR (200 MHz) spectra were recorded on a BRUKER-AC 200 MHz spectrometer. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s=singlet, d=doublet, t=triplet, m=multiplet), coupling constant (Hz). ^{13}C NMR (50 MHz) spectra were recorded on a BRUKER-AC 200 MHz Spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance the internal standard (deuterochloroform: 77.0 ppm). UV/vis absorption spectra were recorded on a Shimadzu UV-2450 UV/vis spectrophotometer, fluorescence emission spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer, FTIR spectra were recorded on a Perkin–Elmer RXI spectrometer, and HRMS spectra were recorded on a JEOL-AccuTOF JMS-T100L mass spectrometer. Photolysis of all the ester conjugates was carried out using 125 W medium pressure mercury lamp supplied by SAIC (India). Chromatographic purification was done with 60–120 mesh silica gel (Merck). For reaction monitoring, precoated silica gel 60 F_{254} TLC sheets (Merck) were used.

4.2. General procedure for the synthesis of caged esters (4a–c)

3-(Bromomethyl)perylene (1 equiv) was dissolved in dry *N*,*N*-dimethylformamide (DMF) (2 ml), potassium iodide (1.2 equiv), potassium carbonate (1.2 equiv) and the corresponding carboxylic acid (1 equiv) were added. The reaction mixture was stirred at room temperature for 8–12 h. The solvent was removed by rotary evaporation under reduced pressure and the crude residue was purified by column chromatography using ethylacetate (EtOAC) in pet. ether.

*4.2.1. (Perylen-3-yl)methyl 2-phenylacetate (**4a**).* 3-(Bromomethyl) perylene (0.100 g, 0.29 mmol), potassium iodide (0.057 g, 0.34 mmol), potassium carbonate (0.048 g, 0.34 mmol), and phenyl acetic acid (0.039 g, 0.29 mmol) were used. The reaction mixture was stirred for 10 h. The crude residue was purified by column chromatography with 20% EtOAc in pet. ether to give the title compound **4a** (0.105 g, 91%) as a yellow solid, mp: 109–112 °C; TLC R_f 0.63 (15% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.21–8.07 (m, 6H), 7.68 (d, *J*=7.4 Hz, 4H), 7.47 (t, *J*=7.2 Hz, 5H), 7.31 (s, 1H), 5.50 (s, 2H), 3.70 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=171.7, 134.7, 134.0, 133.0, 132.3, 131.9, 131.2, 130.8, 129.5, 128.7, 128.3, 128.1, 127.3, 127.1, 126.7, 123.4, 120.6, 120.4, 119.7, 65.3, 41.6; FTIR (KBr, cm^{-1}): 1718; HRMS calcd for $C_{29}H_{20}O_2$: 400.1463, found: 400.1461.

*4.2.2. (Perylen-3-yl)methyl 4-methylbenzoate (**4b**).* 3-(Bromomethyl) perylene (0.100 g, 0.29 mmol), potassium iodide (0.057 g, 0.34 mmol), potassium carbonate (0.048 g, 0.34 mmol), and 4-methyl benzoic acid (0.039 g, 0.29 mmol) were used. The reaction mixture was stirred for 8 h. A reddish-brown residue was obtained which on purification using 25% EtOAc in pet. ether gave compound **4b** (0.102 g, 88%) as a yellow solid, mp: 139–143 °C; TLC R_f 0.68 (15% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.22–8.11 (m, 4H), 7.97 (d, *J*=8.2 Hz, 2H), 7.90 (d, *J*=8.4 Hz, 1H), 7.68 (d, *J*=8.2 Hz, 2H), 7.53–7.43 (m, 4H), 7.22 (d, *J*=8.0 Hz, 2H), 5.71 (s, 2H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=166.6, 143.8, 134.6, 133.1, 132.1, 131.8, 131.1, 130.9, 129.8, 129.1, 128.4, 128.1, 127.4, 127.1, 126.6, 123.4, 120.5, 120.3, 119.6, 65.0, 21.6; FTIR (KBr, cm^{-1}): 1717; HRMS calcd for $C_{28}H_{18}O_2$: 386.1307, found: 386.1306.

*4.2.3. (Perylen-3-yl)methyl 4-methoxybenzoate (**4c**).* 3-(Bromomethyl)perylene (0.100 g, 0.29 mmol), potassium iodide (0.057 g, 0.34 mmol), potassium carbonate (0.048 g, 0.34 mmol), and 4-methoxybenzoic acid (0.044 g, 0.29 mmol) were used. The reaction mixture was stirred for 8 h. A reddish-brown residue was obtained which on purification using 25% EtOAc in pet. ether gave compound **4c** (0.104 g, 86%) as a yellow solid, mp: 151–155 °C; TLC R_f 0.53 (15% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.18 (q, *J*=7.8 Hz, 4H), 8.07 (d, *J*=9.0 Hz, 2H), 7.92 (d, *J*=8.4 Hz, 1H), 7.71 (d, *J*=8.0 Hz, 2H), 7.59–7.45 (m, 4H), 6.93 (d, *J*=9.0 Hz, 2H), 5.72 (s, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=166.3, 163.5, 134.6, 133.0, 132.1, 131.8, 131.2, 131.1, 130.9, 129.2, 128.9, 128.4, 128.0, 127.0, 126.6, 123.4, 122.6, 120.5, 120.3, 119.6, 117.3, 113.7, 112.5, 64.9, 55.4; FTIR (KBr, cm^{-1}): 1700; HRMS calcd for $C_{29}H_{20}O_3$: 416.1412, found: 416.1422.

4.3. General procedure for the synthesis of caged esters (4d–h)

3-(Bromomethyl)perylene (1 equiv) was dissolved in dry DMF (2 ml) and the corresponding Boc-protected amino acid (**3d**–**h**) (1 equiv) was added followed by 1.2 equiv of K_2CO_3 and KF. The reaction mixture was stirred at room temperature for 8–12 h. The solvent was removed by rotary evaporation under reduced pressure and the crude residue was purified by column chromatography with EtOAc in pet. ether as an eluant.

*4.3.1. tert-Butyl (((perylen-3-yl) methoxy) carbonyl) methylcarbamate (**4d**).* 3-(Bromomethyl)perylene (0.100 g, 0.29 mmol), potassium fluoride (0.020 g, 0.34 mmol), potassium carbonate (0.048 g, 0.34 mmol), and *N*-(*tert*-butoxycarbonyl)glycine (0.051 g, 0.29 mmol). The reaction mixture was stirred for 10 h. Crude reaction mixture was purified by column chromatography using 35% EtOAc in pet. ether to give compound **4d** (0.102 mg, 80%) as a light yellow solid, mp: 175–178 °C; TLC R_f 0.75 (30% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.11–7.99 (m, 4H), 7.71 (d, *J*=8.0 Hz, 1H), 7.64 (d, *J*=8.0 Hz, 2H), 7.50–7.38 (m, 4H), 5.49 (s, 2H), 5.04 (s, 1H, NH), 3.95 (d, *J*=4.6 Hz, 2H), 1.42 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=170.5, 155.8, 134.6, 132.9, 132.4, 131.8, 131.0, 130.8, 130.2, 128.9, 128.5, 128.3, 128.1, 127.2, 126.6, 123.2, 120.6, 120.4, 119.5, 80.2, 65.5, 42.6, 28.4; FTIR (KBr, cm^{-1}): 2925, 1761; HRMS calcd for $C_{28}H_{25}NO_4$: 439.1784, found: 439.1791.

*4.3.2. tert-Butyl 3-(((perylen-3-yl) methoxy)carbonyl) propylcarbamate (**4e**).* 3-(Bromomethyl)perylene (0.100 g, 0.29 mmol), potassium fluoride (0.020 g, 0.34 mmol), potassium carbonate (0.048 g, 0.34 mmol), and 4-(*tert*-butoxycarbonylamino)butyric acid (0.059 g, 0.29 mmol) were used. The reaction mixture was stirred for 10 h. A brown solid obtained which on purification by column chromatography using 30% EtOAc in pet. ether gave the cage ester **4e** (0.103 g, 76%) as a yellow solid, mp: 165–168 °C; TLC R_f 0.65 (30% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.31–8.18 (m, 4H), 7.95 (d, *J*=8.6 Hz, 1H), 7.65 (d, *J*=8.2 Hz, 2H), 7.60–7.36 (m, 4H), 5.51 (s, 2H), 4.58 (s, NH), 3.16 (q, *J*=6.6 Hz, 2H), 2.43 (t, *J*=7.4 Hz, 2H), 1.84 (m, 2H), 1.42 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=173.2, 155.9, 134.5, 132.4, 131.8, 131.1, 130.8, 129.3, 128.9, 128.4, 128.1, 127.9, 126.9, 126.6, 126.0,

123.4, 120.5, 120.3, 120.1, 119.5, 79.3, 64.7, 39.9, 31.6, 28.4; FTIR (KBr, cm^{-1}): 2927, 1722; HRMS calcd for $C_{30}H_{29}NO_4$: 467.2097, found: 467.2106.

*4.3.3. tert-Butyl (S)-1-(((perylen-3-yl)methoxy)carbonyl) ethylcarbamate (**4f**).* 3-(Bromomethyl)perylene (0.100 g, 0.29 mmol), potassium fluoride (0.020 g, 0.34 mmol), potassium carbonate (0.048 g, 0.34 mmol), and *N*-(*tert*-butoxycarbonyl)-L-alanine (0.055 g, 0.29 mmol) were used. The reaction mixture was stirred for 12 h. A deep brown solid residue obtained which on purification by column chromatography using 30% EtOAc in pet. ether gave compound **4f** (0.099 mg, 75%) as a yellow solid, mp: 144–147 °C; TLC R_f 0.30 (15% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.24–8.11 (m, 4H), 7.79 (d, *J*=8.2 Hz, 1H), 7.69 (d, *J*=8.2 Hz, 2H), 7.58–7.44 (m, 4H), 5.55 (dd, *J*=12.4, 7.6 Hz, 2H), 5.08 (s, NH), 4.38 (t, *J*=6.8 Hz, 1H), 1.43 (s, 9H), 1.38 (d, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=173.3, 155.0, 134.5, 132.8, 132.3, 131.8, 130.9, 130.7, 130.3, 128.9, 128.4, 128.3, 128.2, 128.0, 127.9, 127.1, 126.6, 126.5, 123.1, 120.6, 120.5, 120.3, 119.5, 79.8, 65.5, 49.3, 28.2, 18.6; FTIR (KBr, cm^{-1}): 2924, 1711; HRMS calcd for $C_{29}H_{27}NO_4$: 453.1940, found: 453.1948.

*4.3.4. tert-Butyl (S)-1-(((perylen-3-yl)methoxy)carbonyl)-2-phenylethylcarbamate (**4g**).* 3-(Bromomethyl)perylene (0.100 g, 0.29 mmol), potassium fluoride (0.020 g, 0.34 mmol), potassium carbonate (0.048 g, 0.34 mmol), and *N*-(*tert*-butoxycarbonyl)-L-phenylalanine (0.077 g, 0.29 mmol) were used. The reaction mixture was stirred for 12 h. The crude reaction mixture was purified by column chromatography using 25% EtOAc in pet. ether to give ester conjugate **4g** (0.121 mg, 79%) as a yellow solid, mp: 147–150 °C; TLC R_f 0.30 (15% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.28–8.18 (m, 3H), 8.12 (d, *J*=7.8 Hz, 1H), 7.76–7.68 (m, 3H), 7.56–7.45 (m, 4H), 7.14 (s, 3H), 6.98 (s, 2H), 5.52 (dd, *J*=12.4, 4.0 Hz, 2H), 4.98 (d, *J*=8.8 Hz, NH), 4.659–4.629 (m, 1H), 3.05 (d, *J*=5.4 Hz, 2H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=171.9, 154.8, 135.8, 134.6, 133.0, 132.5, 131.9, 131.0, 130.8, 130.2, 129.3, 129.0, 128.7, 128.5, 128.3, 128.1, 127.2, 126.9, 126.7, 123.3, 120.6, 120.4, 119.5, 79.9, 65.5, 54.5, 38.4, 28.3; FTIR (KBr, cm^{-1}): 2925, 1733; HRMS calcd for $C_{35}H_{31}NO_4$: 529.2253, found: 529.2368.

*4.3.5. tert-Butyl(S)-1-(((perylen-3-yl)methoxy)carbonyl)-2-(1H-indol-3-yl)ethylcarbamate (**4h**).* 3-(Bromomethyl)perylene (0.100 g, 0.29 mmol), potassium fluoride (0.020 g, 0.34 mmol), potassium carbonate (0.048 g, 0.34 mmol), and *N*-(*tert*-butoxycarbonyl)-L-tryptophan (0.088 g, 0.29 mmol) were used. The reaction mixture was stirred for 12 h. The crude reaction mixture was purified by column chromatography using 30% EtOAc in pet. ether to give caged ester **4h** (0.135 mg, 82%) as a yellow solid, mp: 162–164 °C; R_f 0.50 (30% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.27–8.16 (m, 3H), 8.11 (d, *J*=7.6 Hz, 1H), 7.75–7.60 (m, 3H), 7.52–7.34 (m, 4H), 7.20–7.06 (m, 4H), 6.69 (s, 1H), 5.48 (dd, *J*=12.2, 6.2 Hz, 2H), 5.11 (s, 1H), 4.74 (m, 1H), 3.27 (d, *J*=5.0 Hz, 2H), 1.42 (s, 9H), ^{13}C NMR ($CDCl_3$, 50 MHz): δ=172.3, 155.2, 136.0, 134.6, 132.9, 132.2, 131.7, 131.0, 130.8, 130.3, 129.6, 128.98, 128.5, 128.2, 128.0, 127.6, 127.1, 126.6, 123.2, 122.8, 122.1, 120.6, 120.3, 119.6, 119.5, 118.7, 111.1, 109.9, 79.9, 65.4, 54.4, 29.9, 28.3; FTIR (KBr, cm^{-1}): 2926, 1706; HRMS calcd for $C_{37}H_{32}N_2O_4$: 568.2362, found: 568.2479.

4.4. General procedure for the synthesis of caged carbonates (7a–d)

3-(Hydroxymethyl)perylene (1 equiv) was dissolved in dry DCM (5 ml), and to the solution corresponding alcohol chloroformate (1 equiv) was added followed by 1.2 equiv of *N*,*N*-dimethylpyridin-4-amine (DMAP). The reaction mixture was stirred at room temperature for 8–10 h. The solvent was removed by rotary evaporation under reduced pressure and the crude residue was purified by column chromatography with EtOAc in pet. ether as an eluant.

*4.4.1. Cyclohexyl (perylen-3-yl)methyl carbonate (**7a**).* 3-(Hydroxymethyl)perylene (0.100 g, 0.36 mmol), cyclohexyl chloroformate (0.059 g, 0.36 mmol), and DMAP (0.053 g, 0.43 mmol) were used and the reaction mixture was stirred for 6 h at room temperature. The crude reaction mixture was purified by column chromatography using 10% EtOAc in pet. ether to give the carbonate ester **7b** (0.112 mg, 76%) as a yellow solid, mp: 158–160 °C; TLC R_f 0.60 (15% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.23–8.10 (m, 4H), 7.86 (d, *J*=8.2 Hz, 1H), 7.69 (d, *J*=8.0 Hz, 2H), 7.58–7.43 (m, 4H), 5.54 (s, 2H), 4.71–4.62 (m, 1H), 1.98–1.26 (m, 10H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=154.9, 134.7, 133.1, 132.5, 131.9, 131.2, 130.9, 130.6, 129.1, 128.5, 128.3, 128.1, 127.3, 126.7, 123.4, 120.7, 120.5, 119.7, 72.8, 67.74, 31.7, 25.4, 23.9; FTIR (KBr, cm^{-1}): 1734; HRMS calcd for $C_{28}H_{24}O_3$: 408.1725, found: 408.1727.

*4.4.2. 2-Isopropyl-5-methylcyclohexyl (perylen-3-yl)methyl carbonate (**7b**).* 3-(Hydroxymethyl)perylene (0.100 g, 0.36 mmol), menthol chloroformate (0.079 g, 0.36 mmol), and DMAP (0.053 g, 0.43 mmol) were used and the reaction mixture was stirred for 8 h at room temperature. The crude reaction mixture was purified by column chromatography using 10% EtOAc in pet. ether to give the carbonate ester **7c** (0.125 mg, 75%) as a yellow solid, mp: 132–135 °C; TLC R_f 0.72 (15% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.17–8.05 (m, 4H), 7.79 (d, *J*=8.4 Hz, 1H), 7.64 (d, *J*=8.2 Hz, 2H), 7.52–7.39 (m, 4H), 5.51 (s, 2H), 4.62–4.49 (m, 1H), 2.10–1.88 (m, 3H), 1.67–1.60 (2H), 1.40 (m, 1H), 1.11–0.994 (m, 3H), 0.89–0.83 (m, 6H), 0.76 (d, *J*=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=155.0, 134.5, 132.8, 132.2, 131.7, 131.0, 130.8, 130.4, 128.9, 128.4, 128.1, 127.9, 127.0, 126.5, 123.2, 120.5, 120.3, 119.5, 78.8, 67.7, 47.1, 40.8, 34.1, 31.5, 26.1, 23.4, 22.0, 20.7, 16.3; FTIR (KBr, cm^{-1}): 1736; HRMS calcd for $C_{32}H_{32}O_3$: 464.2351, found: 464.2348.

*4.4.3. (8S,9S,10R,13R,14S,17R)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-Tetradecahydro-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-1H-cyclopenta[a]phenanthren-3-yl (perylen-3-yl)methyl carbonate (**7c**).* 3-(Hydroxymethyl)perylene (0.100 g, 0.36 mmol), cholesterol chloroformate (0.162 g, 0.36 mmol), and DMAP (0.053 g, 0.43 mmol) were used and the reaction mixture was stirred for 6 h at room temperature. The crude reaction mixture was purified by column chromatography using 10% EtOAc in pet. ether to give the carbonate ester **7d** (0.198 mg, 79%) as a yellow solid, mp: 168–170 °C; TLC R_f 0.72 (15% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.20–8.08 (m, 4H), 7.83 (d, *J*=8.4 Hz, 1H), 7.66 (d, *J*=8.0 Hz, 2H), 7.55–7.40 (m, 4H), 5.51 (s, 2H), 5.35 (d, *J*=4.0 Hz, 1H), 4.59–4.43 (m, 1H), 2.39–2.34 (m, 2H), 1.98–1.09 (m, 23H), 0.95 (s, 6H), 0.89–0.82 (m, 9H), 0.63 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=154.6, 139.3, 134.5, 132.8, 132.2, 131.6, 130.9, 130.7, 130.2, 128.8, 128.4, 128.2, 127.9, 127.0, 126.5, 123.2, 122.9, 120.5, 120.2, 119.4, 78.2, 71.8, 67.6, 56.6, 56.1, 49.9, 42.3, 39.7, 39.5, 38.1, 36.8, 36.5, 36.2, 35.8, 31.81, 28.2, 28.0, 27.7, 24.3, 23.9, 22.9, 22.6, 21.0, 19.2, 18.7; FTIR (KBr, cm^{-1}): 1741; HRMS calcd for $C_{49}H_{58}O_3$: 694.4386, found: 694.4388.

*4.4.4. (Perylen-4-yl)methyl phenyl carbonate (**7d**).* 3-(Hydroxymethyl)perylene (0.100 g, 0.36 mmol), phenyl chloroformate (0.056 g, 0.36 mmol), and DMAP (0.053 g, 0.43 mmol) were used and the reaction mixture was stirred for 10 h at room temperature. The crude reaction mixture was purified by column chromatography using 15% EtOAc in pet. ether to give the carbonate ester **7e** (0.119 mg, 82%) as a yellow solid, mp: 130–132 °C; TLC R_f 0.48 (15% EtOAc in pet. ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.22–8.09 (m, 4H), 7.88 (d, *J*=8.2 Hz, 1H), 7.67 (d, *J*=8.0 Hz, 2H), 7.63–7.15 (m, 9H),

5.54 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=153.9, 151.4, 134.7, 132.9, 132.7, 131.9, 131.1, 130.8, 129.8, 129.7, 128.8, 128.4, 128.2, 127.3, 126.7, 126.4, 126.5, 126.3, 123.2, 121.3, 121.1, 120.8, 120.7, 120.5, 119.5, 68.9; FTIR (KBr, cm^{-1}): 1744; HRMS calcd for $C_{28}H_{18}O_3$: 402.1256, found: 402.1260.

4.5. Photophysical properties of caged esters (4a–h) and carbonates (7a–d)

The UV/vis absorption spectra of degassed 2×10^{-6} M solution of the caged esters (**4a**–**h**) and carbonates (**7a**–**d**) in absolute ethanol were recorded on a Shimadzu UV-2450 UV/vis spectrophotometer, and the fluorescence emission spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. Fluorescence quantum yield of the caged compounds was calculated using the Eq. 1.[23]

$$\left(\Phi_f\right)_{CG} = \left(\Phi_f\right)_{ST}\frac{(Grad_{CG})}{(Grad_{ST})}\frac{(\eta^2_{CG})}{(\eta^2_{ST})} \quad (1)$$

where, the subscript CG and ST denotes caged compound and standard, respectively. 9,10-Diphenylanthracene in ethanol was taken as standard. Φ_f is fluorescence quantum yield; Grad is the gradient from the plot of integrated fluorescence intensity versus absorbance, and η the refractive index of the solvent.

Since, fluorescence for both caged compounds and standard were recorded in the same solvent Eq. 1a was used for the calculation of fluorescence quantum yield.

$$\left(\Phi_f\right)_{CG} = \left(\Phi_f\right)_{ST}\frac{(Grad_{CG})}{(Grad_{ST})} \quad (1a)$$

4.6. Deprotection photolysis of caged esters (4a–h) and carbonates (7a–d)

A solution of 10^{-4} M of the caged esters (**4a**–**h**) and carbonates (**7a**–**d**) was prepared in acetonitrile/H_2O (75/25) individually. Half of the solution was kept in dark and to the remaining half nitrogen was passed and irradiated using 125 W medium pressure Hg lamp as visible light source ($\geq$410 nm) and 1 M $NaNO_2$ solution as UV cut-off filter. At regular interval of time, 20 μl of the aliquots was taken and analyzed by RP-HPLC using mobile phase methanol, at a flow rate of 1 ml/min (detection: UV 254 nm). Peak areas were determined by RP-HPLC, which indicated gradual decrease of the caged compound with time, and the average of three runs. The reaction was followed until the consumption of the caged compound is less than 5% of the initial area. Based on HPLC data for each caged compounds, we plotted normalized [*A*] (HPLC peak area) versus irradiation time. We observed an exponential correlation for the disappearance of the caged compounds, which suggested a first order reaction. Further, the quantum yield for the photolysis of caged compounds was calculated using Eq. 2

$$(\Phi_p)_{CG} = \frac{(k_p)_{CG}}{I_0(F_{CG})} \quad (2)$$

where, the subscript 'CG' denotes caged compound. Φ_p is the photolysis quantum yield, k_p is the photolysis rate constant, and I_0 is the incident photon flux and F is the fraction of light absorbed. Potassium ferrioxalate was used as an actinometer.

4.7. Determination of incident photon flux (I_0) of the UV lamp by potassium ferrioxalate actinometry

Potassium ferrioxalate actinometry[19,20] was used for the determination of incident photon flux (I_0) of the UV lamp used for irradiation. Solution of potassium ferrioxalate, 1,10-phenanthroline and the buffer solution were prepared following the literature procedure.[19]

Solution (0.006 M) of potassium ferrioxalate was irradiated using 125 W medium pressure Hg lamp as visible light source ($\geq$410 nm) and 1 M $NaNO_2$ solution as UV cut-off filter. At regular interval of time (3 min), 1 ml of the aliquots was taken out and to it 3 ml of 1,10-phenanthroline solution and 2 ml of the buffer solution were added and the whole solution was kept in dark for 30 min. The absorbance of red phenanthroline–ferrous complex formed was then measured spectrophotometrically at 510 nm. The amount of Fe^{2+} ion was determined from the calibration graph. The calibration graph was plotted by measuring the absorbance of phenanthroline–ferrous complex at several known concentration of Fe^{2+} ion in dark. From the slope of the graph the molar absorptivity of the phenanthroline–ferrous complex was calculated to be 1.10×10^4 M^{-1} cm^{-1} at 510 nm, which is found to be similar to reported value.[19a] Using the known quantum yield for potassium ferrioxalate actinometer at 406.7 nm,[24] the number of Fe^{2+} ion formed during photolysis and the fraction of light absorbed by the actinometer, the incident intensity (I_0) of the 125 W Hg lamp was determined as 5.767×10^{17} quanta S^{-1}.

4.8. Preparative photolysis

A solution of caged compound (**4a**–**h**) and (**7b**–**d**) (0.05 mmol) in acetonitrile/H_2O (75/25) individually was irradiated using the procedure described under deprotection photolysis. The irradiation was monitored by TLC at regular intervals. After completion of photolysis, solvent was removed under vacuum and the photoproducts (3-(hydroxymethyl)perylene, and the corresponding carboxylic acid or alcohol) were isolated by column chromatography using increasing percentage of EtOAc in hexane as an eluant.

3-(Hydroxymethyl)perylene (**1**): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.23 (m, 4H), 7.93 (d, *J*=8.6 Hz, 1H), 7.72 (d, *J*=7.8 Hz, 2H), 7.56–7.33 (m, 4H), 5.07 (s, 2H).

A solution of caged compound (**4c**) (0.05 mmol) in MeOH/H_2O (95/5 v/v) was photolysed and the irradiation was monitored by HPLC at regular intervals. After completion of photolysis, solvent was removed under vacuum and the photoproducts (3-(methoxymethyl)perylene and 4-methoxybenzoic acid) were isolated by column chromatography using increasing percentage of EtOAc in hexane as an eluant.

3-(Methoxymethyl)perylene: ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.23–8.14 (m, 4H), 7.94 (d, *J*=8.2 Hz, 1H), 7.69 (d, *J*=8.2 Hz, 2H), 7.58–7.44 (m, 4H), 4.85 (s, 2H), 3.48 (s, 3H).

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.11.074.

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