PAPER

1-Acetylferroceneoxime-based photoacid generators: application towards sol–gel transformation and development of photoresponsive polymer for controlled wettability and patterned surfaces†

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A newsworthy class of carboxylate and sulfonate esters of 1-acetylferroceneoxime has been demonstrated as non-ionic photoacid generators (PAGs). PAGs based on 1-acetylferroceneoxime were synthesized in good yields by simple treatment of 1-acetylferroceneoxime with various carboxylic and sulfonyl chlorides. Newly developed PAGs of 1-acetylferroceneoxime showed good absorbance >350 nm. On irradiation using UV light (≥365 nm), carboxylates and sulfonates of 1-acetyl ferroceneoxime in aqueous acetonitrile solvent underwent efficient homolytic cleavage of N−O bond, resulting in the generation of carboxylic and sulphonic acids, respectively, with high chemical and good quantum yields. Further, we demonstrated the application of our newly developed 1-acetylferroceneoxime-based PAGs for gelation of biopolymer alginate on UV irradiation. More interestingly, we synthesized a ferroceneoxime bound photoresponsive polymer, 1-acetylferroceneoxime-polycaprolactone (AFO-PCL), and demonstrated its controlled surface wettability and generation of patterned surfaces.

Introduction

Recently, application of external stimuli, such as light, solvent, pH, or an electric field, for tuning surface properties has captured great attention.[1] In comparison to other external stimuli, light offers excellent spatial and temporal control over the energy input required for tuning surface properties.[2] Hence, several photoresponsive materials were developed and their surface properties such as wetting behavior, adhesion, and adsorption were demonstrated to be easily tuned by external stimulus light.[3]

In particular, the design of photoresponsive materials with controlled wettability has become as an exciting topic from the viewpoint of both fundamental scientific theory and practical applications.[4] Several research groups have developed photoresponsive materials with controlled wettability[3] by using everything from inorganic nanomaterials[5] to small organic molecules[6] and photoactive polymers.[7] In comparison with inorganic materials, organic materials have many advantages in terms of the number of adaptable species, the capability of

chemical modification, and reaction diversity.[8] Though organic materials have the above advantages, they lack the intrinsic properties possessed by inorganic materials such as good chemical and mechanical stability, low cost, and outstanding photo/electro-properties.[9] Hence, photoresponsive organic–inorganic hybrid materials exhibiting both inorganic and organic properties were developed.[10] Generally, photoresponsive hybrid materials are bicomponent systems, and they are prepared by combining both organic and inorganic building blocks.[11] The major concern with the bicomponent system is loading inefficiency of inorganic material on organic component or *vice versa*. By any means if we can develop photoresponsive compounds containing both inorganic and organic nature, then we can eliminate the above loading inefficiency.

Ferrocene, namely cyclopentadienyl iron with the chemical formula of $Fe(C_5H_5)_2$, is one of the most studied and versatile organometallic building blocks. It is of considerable interest in various areas, like asymmetric catalysis,[12] non-linear optics[13] and electrochemistry[14] due to the quasi-reversible oxidation[15] of iron II. In addition, ferrocene photochemical behaviour has also been well studied.[16] Although they are often photochemically inert, ferrocene and ferrocenyl derivatives undergo chemical modifications in the presence of light.[17] They are also used as excited state quenchers or photosensitizers.[18] Moreover, a ferrocene moiety also provides the capability of chemical modification and reaction diversity.[19] Inspired by the ability of

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ferrocenyl derivatives to exhibit both inorganic and organic properties, we were prompted to design single component photoresponsive materials based on a ferrocene moiety.

We have recently become interested in imparting photoresponsiveness to materials using a photoacid generator (PAG). PAGs are commercially available molecules that have been used for a long time in the microelectronics industry.[20] Their distinctive property is that they get photolyzed by UV light to form an acidic moiety. Accordingly, we have constructed photoresponsive materials by imparting PAGs like 1-hydroxy-2(1H)-quinolone[21] and N-hydroxyanthracene-1,9-dicarboxyimide.[22] Further, we also demonstrated the switchable wettability behavior of the above photoresponsive materials with a large change in contact angle (CA) from hydrophobic to hydrophilic. Hence, we thought to design for the first time new PAGs based on 1-acetylferroceneoxime and use them in the construction of photoresponsive materials.

In the present study, we have described the synthesis and characterization of 1-acetylferroceneoxime-based PAGs. We examined the acid generation ability of PAGs by irradiating with UV light above 365 nm and demonstrated the application of the acid generation ability of PAGs in sol–gel transformation of the biopolymer alginate. Further, we constructed the photoresponsive polymer acetylferroceneoxime-polycaprolactone (AFO-PCL) using ring-opening polymerization (ROP). Moreover, we also investigated the photoresponsive behaviour of the above synthesized polymer in terms of controlled wettability and generation of patterned surfaces.

Results and discussion

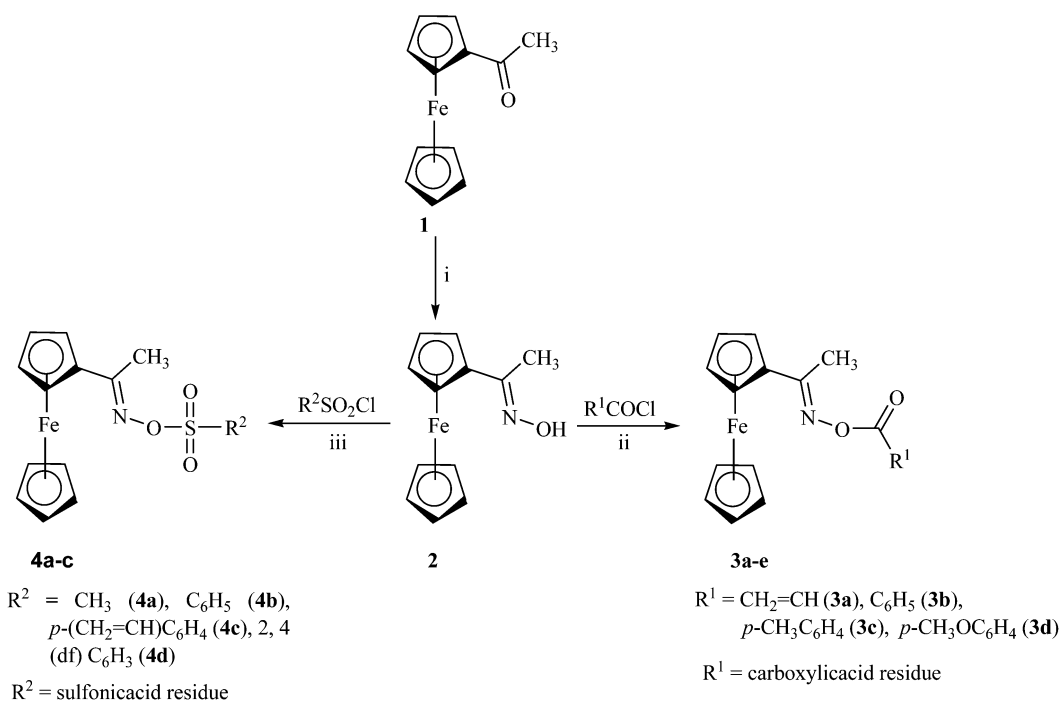### Carboxylates and sulfonates of (E)-1-acetylferroceneoxime as PAGs

Synthesis of PAGs (3a–d and 4a–d). 1-Acetylferroceneoxime (2) was initially prepared by condensation of 1-acetylferrocene (1)[23] with hydroxylamine hydrochloride in ethanol at reflux condition.[24] Later, treatment of 2 with various acid chlorides and sulfonyl chlorides in the presence of 2 equiv. triethylamine in dry DCM at 0 °C for a period of 12–18 h afforded corresponding carboxylates (3a–d) and sulfonates (4a–d), with good yields (75–85%, Table 1) (Scheme 1). All the carboxylates and sulfonates were purified and characterized by ^{1}H, ^{13}C NMR, IR and mass spectral analysis.

UV-vis study of PAGs (3a–d and 4a–d). UV-vis absorption of 1 × 10^{-4} M solution of PAGs (3a–d and 4a–d) (carboxylate and sulfonate esters) was recorded in methanol and their corresponding UV-vis spectra are shown in Fig. 1a and 1b. The

Table 1 Reaction time and synthetic yield of PAGs (3a–d and 4a–d)

PAGs	Acid chloride	Reaction time (h)	Yield^a (%)
3a	CH$_2$=CHCOCl	15	82
3b	C$_6$H$_5$COCl	12	80
3c	p-MeC$_6$H$_4$COCl	12	84
3d	p-MeOC$_6$H$_4$COCl	15	85
4a	CH$_3$SO$_2$Cl	15	80
4b	C$_6$H$_5$SO$_2$Cl	18	81
4c	P(CH$_2$=CH)C$_6$H$_4$SO$_2$Cl	18	80
4d	2,4(df)C$_6$H$_3$SO$_2$Cl	18	75

^{a} Based on isolated yield.

4a-c

R^2 = CH$_3$ (**4a**), C$_6$H$_5$ (**4b**), p-(CH$_2$=CH)C$_6$H$_4$ (**4c**), 2, 4 (df) C$_6$H$_3$ (**4d**)

R^2 = sulfonicacid residue

3a-e

R^1 = CH$_2$=CH (**3a**), C$_6$H$_5$ (**3b**), p-CH$_3$C$_6$H$_4$ (**3c**), p-CH$_3$OC$_6$H$_4$ (**3d**)

R^1 = carboxylicacid residue

Scheme 1 Synthesis of PAGs (3a–d) and (4a–d). Reagents and conditions: (i) NH$_2$OH.HCl, EtOH, reflux, (ii) and (iii) Et$_3$N, 0 °C-rt, dry DCM, 12–18 h.

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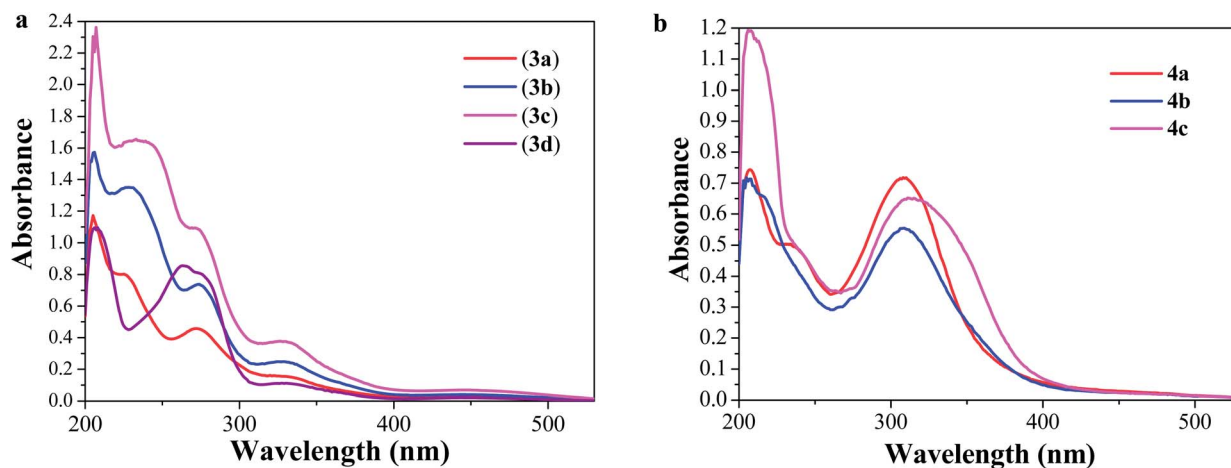*J. Mater. Chem. C*, 2014, **2**, 4622–4630 | **4623**

Fig. 1 (a) UV-vis absorption spectra of carboxylate esters (3a–d). (b) UV-vis absorption spectra of sulfonate esters (4a–c).

Table 2 UV-vis absorption data of PAGs (3a–d and 4a–d)

| | UV-vis absorption | |
PAGs	$\lambda_{max}{}^a$ (nm)	$\log \varepsilon^b$
3a	320	3.20
3b	325	3.39
3c	330	3.57
3d	328	3.04
4a	327	3.75
4b	328	3.64
4c	329	3.79
4d	329	3.77

[a] Maximum absorption wavelength. [b] Molar absorption coefficient.

Table 3 Photolysis of PAGs (3d) in various solvents

Solvent system	% of acid generated[a]	Quantum yield[b] (Φ_p)
MeOH	80	0.074
ACN	65	0.060
THF[c]	—	—
CHCl₃[c]	—	—
Benzene[c]	—	—
MeOH–H₂O (95 : 1)	90	0.083
ACN–H₂O (95 : 1)	80	0.074

[a] Photolysis yield based on HPLC. [b] Quantum yield for the generation of p-anisic acid at room temperature (error limit within ±5%). [c] Polymeric products were observed.

absorption maxima and molar absorptivities of the above esters are summarized in Table 2.

The UV-vis absorption data showed that all the carboxylate and sulfonate esters exhibited good UV absorption near 350 nm, indicating that the photolysis can be carried out using UV light above 350 nm.

Solvent effect on the photogeneration of acid by PAG (3d). To identify the right solvent required for the effective generation of acids from their corresponding PAGs, we carried out photolysis of **3d** (1.0×10^{-4} M) in various solvents including methanol (MeOH), acetonitrile (ACN), tetrahydrofuran (THF), chloroform (CHCl₃), benzene, MeOH–H₂O (95 : 1) and ACN–H₂O (95 : 1) for 70 min under UV light (≥365 nm) by 125 W medium pressure Hg lamp using a suitable filter (1 M CuSO₄ solution in 0.1 N H₂SO₄), and the results are tabulated in Table 3. We found carboxylate (**3d**) generated p-anisic acid in relatively high quantum and chemical yield in MeOH–H₂O (95 : 1) compared to other solvents used for the study. In other solvents such as THF, CHCl₃ and benzene, polymeric products were also observed.

**Photolysis of PAGs (3a–d and 4a–d).** Based on the above solvent study, we photolysed the carboxylate and sulfonate esters of 1-acetylferroceneoxime (**3a–d** and **4a–d**) in MeOH–H₂O (95 : 1) using UV light (≥365 nm) as shown in Scheme 2.

We found that all the PAGs generated their corresponding acids (**5a–d** and **6a–d**) and 1-acetylferrocene (**1**) in nearly quantitative yield as tabulated in Table 4. In each case, the photolysis was stopped when conversion reached at least 90% (as indicated by HPLC). For all the esters, their photoproducts (carboxylic or sulfonic acid and 1-acetylferrocene) were isolated and characterized by ¹H NMR spectra and compared with their corresponding authentic samples. Quantum yields for the generation of various carboxylic and sulfonic acids were found to be in the range of 0.097 to 0.051 using valerophenone as an actinometer.[25]

As a representative example, we have represented the UV-vis absorption (Fig. 2) spectra of carboxylate ester **3d** at regular intervals of irradiation time.

Mechanism for the photogeneration of carboxylic and sulfonic acids

Based on the mechanistic studies as reported by Scaiano and his coworkers[27] and Shirai et al.[28] for the photolysis of oxime sulfonates and from our solvent investigation, we proposed the possible mechanism for the photogeneration of acids. On
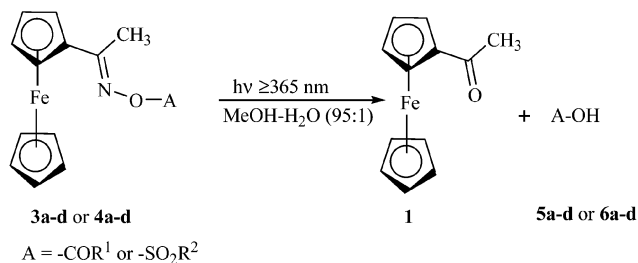
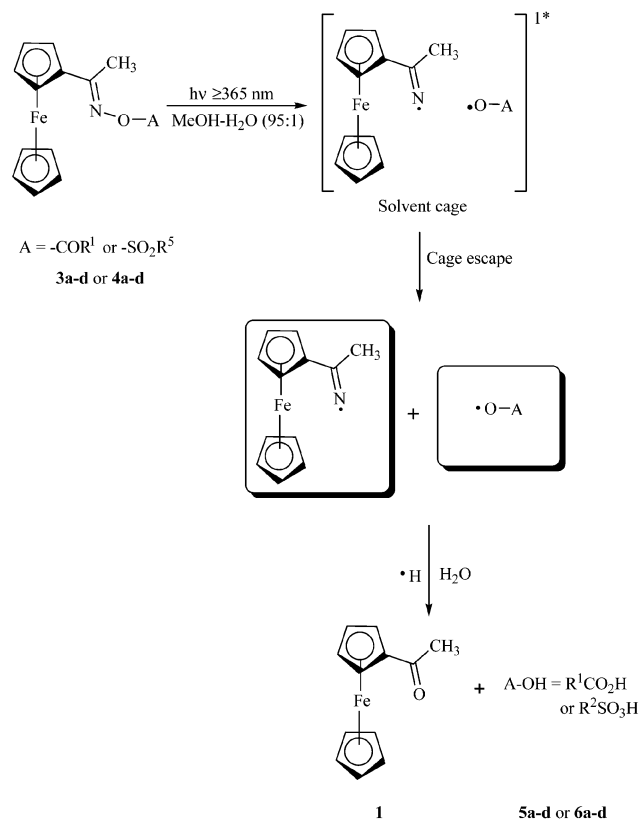**Scheme 2** Photogeneration of acids (**5a–d** or **6a–d**) by PAGs.

Table 4 Photolysis data of the carboxylate and sulfonate esters of (*E*)-1-acetylferroceneoxime (**3a–d** and **4a–d**)

	Photogeneration of acids		
PAGs	Time of photolysis[a] (min)	Yield[b] (A–OH)	Quantum yield[c] (Φ_p)
3a	100	80	0.051
3b	85	80	0.060
3c	80	85	0.068
3d	70	90	0.083
4a	80	85	0.068
4b	60	90	0.097
4c	70	82	0.075
4d	75	80	0.071

[a] Photolysis time. [b] Photolysis yield based on ^{1}H NMR. [c] Quantum yield for the generation of various acids at room temperature (error limit within ±5%). The literature reported quantum yields for naphthalimide photoacid generators is ~0.18–0.20.[26]
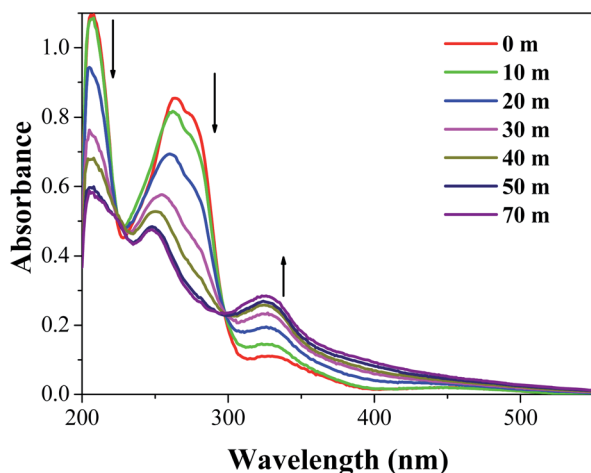
Fig. 2 UV-vis of **3d** (1.0×10^{-4} M) at regular intervals of irradiation time in MeOH–H_2O.

excitation, both the carboxylates and sulfonates of 1-acetylferroceneoxime (**3a–d** and **4a–d**) undergo homolytic N–O bond cleavage from the singlet excited state to generate an iminyl and acyloxy or sulfonyl radical pair (Scheme 3). The above generated radical pair in aqueous polar protic solvent escapes from the cage and subsequently abstracts a hydrogen

Scheme 3 Mechanism for the photogeneration of acids.

atom from the solvent to produce the corresponding carboxylic or sulfonic acid (**5a–d** or **6a–d**) and 1-acetylferrocene (**1**).

After successful demonstration of carboxylate and sulfonate esters of 1-acetylferroceneoxime as PAGs, we focused our attention on the application of the PAGs.

Application of PAGs based on 1-acetylferroceneoxime towards sol–gel transformation and development of photoresponsive polymer surfaces for controlled wettability

Application of PAGs based on 1-acetylferroceneoxime for sol–gel transition. To investigate the ability of our newly developed PAGs in sol–gel transition, we carried out photogelling of well-known biopolymer alginate as described by Raghavan *et al.*[29] We prepared a sample of 2 wt% sodium alginate, 30 mM solubilized PAG in minimum amount of DMSO (**4a**), and 15 mM dispersed $CaCO_3$ particles. Using sonication, these particles were homogeneously dispersed in the polymer solution. We did not observe any type of aggregation or settling of the particles over a period of several hours after sonication. As shown in Fig. 3, the initial mixture is a low-viscosity sol. After exposure to UV light for 30 min, the PAG gets photolyzed, generating sulphonic acid. The generated sulphonic acid reacts with the insoluble $CaCO_3$ particles to produce free Ca^{2+} ions, which cross-link the alginate chains into a gel network. The resulting alginate gel was found to be good enough to hold its weight in the inverted vial (Fig. 3).
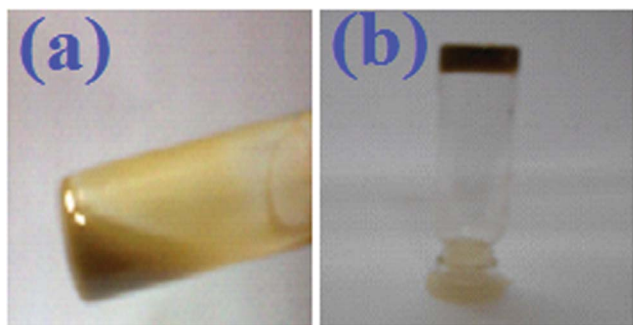
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Fig. 3 Schematic and visual depiction of UV-induced alginate photogelation. Sodium alginate (2 wt%) is combined with 15 mM of $CaCO_3$ particles (insoluble) and 30 mM of a photoacid generator (PAG) (a) before photolysis (b) after photolysis.

Fig. 4 GPC data of copolymer AFO-PCL (**8**).

Development of photoresponsive polymer surfaces using PAG based on 1-acetylferroceneoxime for controlled wettability
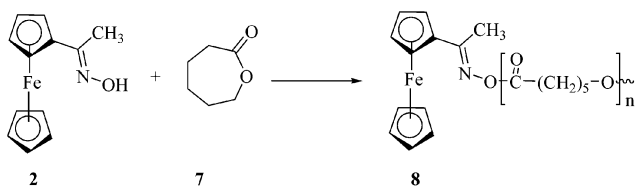
(*E*)-1-Acetylferroceneoxime based polymer 1-acetylferroceneoxime-polycaprolactone (AFO-PCL)] as photoacid generators for carboxylic acid. The copolymer AFO-PCL (**8**) was synthesized by the reaction of (*E*)-1-acetylferroceneoxime (**2**) with ξ-caprolactone (**7**) in presence of $Sn(Oct)_2$ as catalyst using ring-opening polymerization (ROP) technique[30] as shown in Scheme 4.

Characterization of the copolymer AFO-PCL (8)

The molecular weight and polydispersity of the polymer (**8**) were recorded by gel permeation chromatography (GPC). GPC (Fig. 4) was carried out at ambient temperature using a Viscotek-GPC system equipped with two GMH HR-H nonpolar organic columns in series. Tetrahydrofuran was used as an eluent at a flow rate of 1 mL min^{-1}. Polystyrene standards in the M_n range of 955–3 715 000 was used for calibrations.

Photogeneration of acid by copolymer AFO-PCL (8)

To investigate the polymer (**8**) as PAG, it was spin coated onto a glass slide. The polymer film was then baked at 90 °C for a few min in a hot oven. Irradiation of the polymer thin films at ≥365 nm by the use of 125 W medium pressure Hg lamp at room temperature resulted in homolytic cleavage of N–O bond, leading to the generation of acid (Scheme 5).

Scheme 4 Synthesis of copolymer (*E*)-1-acetylferroceneoxime-polycaprolactone (AFO-PCL) (**8**). Reagents and conditions: dry tolune, $Sn(Oct)_2$, 100 °C, 16 h.
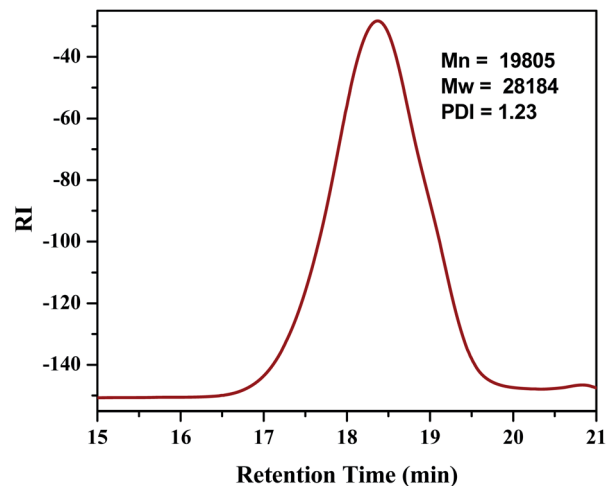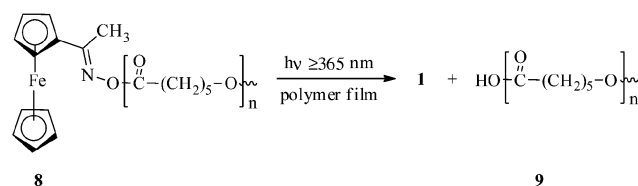

Scheme 5 Photogeneration of acid from polymer film.

The photolysis of the polymer was monitored by IR spectral study at different time interval (see ESI, Fig. S1†).We noticed the peak at 1780 cm^{-1} (ν=CO) due to carbonyl group decreased on irradiation, indicated the photodecomposition of the polymer. On the other hand, the generation of **9** was confirmed by acid-catalyzed polysiloxane formation technique.[31] FT-IR spectra (Fig. S2†) showed changes of irradiated film before and after treatment with methyltriethoxysilane (MTEOS). The appearance of new peaks at 780 (Si–CH₃), 900 (Si–OH), 1000–1200 (Si–O–Si) and 3200–3500 (Si–OH) on irradiation of film showed the formation of silanol, obtained on hydrolysation of MTEOS under humid conditions by newly generated acid.

Investigation of surface photoreactions

To investigate the photoresponsive surface[32] property of our synthesized polymer, we prepared thin polymeric surfaces on the glass wafer and measured the water contact angle (CA). The surface showed a water-contact angle of CA ≈ 145° before UV irradiation, indicating that the surface is hydrophobic in nature (Fig. 5).

The roughness and trapped air[33] are responsible factors of the polymer for the observed hydrophobicity (Fig. 6a), but the surface loses its hydrophobicity and becomes hydrophilic in nature upon direct UV light irradiation (≥365 nm; Fig. 6b). After irradiation, water droplets spread out on the surface, resulting in a contact angle of ≈35°. On photolysis the polymer decomposes and generates polar –CO_2H.

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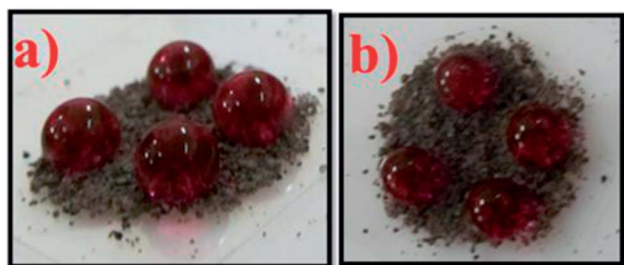This journal is © The Royal Society of Chemistry 2014

Fig. 5 (a) Side view (b) and upper view of water droplet on the polymeric material before photolysis.
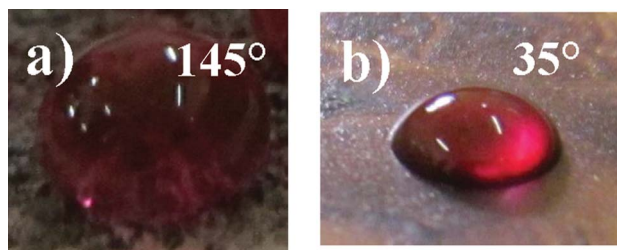

Fig. 6 Water drop on (a) a hydrophobic surface before UV irradiation and (b) a hydrophilic surface on UV irradiation.
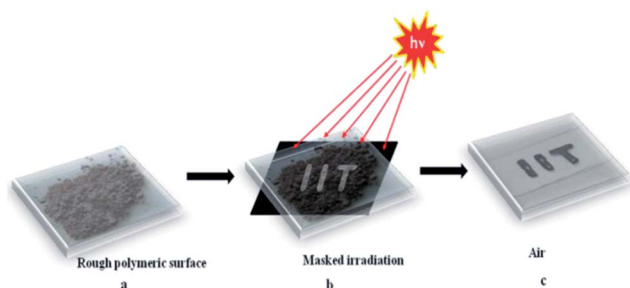

Fig. 7 Photolithographic structuring methods using masked irradiation and polymeric material.

Development of photopattern on the polymeric surface AFO-PCL

Finally, we created patterned films using our photoresponsive polymer AFO-PCL.

The patterning procedure is illustrated schematically in Fig. 7. The polymer (**AFO-PCL** copolymer) layer was smeared on the glass wafer (Fig. 7a). After exposing the polymer surface to UV light (≥365 nm) through a homemade photomask or stencil (Fig. 7b), the patterned was created (Fig. 7c).

Conclusion

We have introduced for the first time carboxylates and sulfonates of 1-acetylferroceneoxime as nonionic photoacid generators (PAGs). Irradiation of carboxylates and sulfonates of 1-acetylferroceneoxime in aqueous methanol at ≥365 nm results in generation of corresponding carboxylic and sulfonic acids in

good quantum yields. More interestingly, we also synthesized a ferroceneoxime-based photoresponsive polymer, namely, 1-acetylferroceneoxime-polycaprolactone (AFO-PCL), and demonstrated its surface wettability. Finally, we used our photoresponsive polymer for the development of patterns on a glass surface.

Experimental section

Chemicals and starting materials

All starting materials, reagents, and solvents were obtained from commercial sources and used without further purification unless otherwise stated. All anhydrous reactions were performed under a dry nitrogen atmosphere.

Methods and techniques

^{1}H NMR (200 MHz) spectra were recorded on a BRUKER-AC 200 MHz spectrometer. Chemical shifts are reported in ppm 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, q = quartet, dd = doublet of doublet, 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 ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 77.0 ppm). Chromatographic purification was done with 60–120 mesh silica gels (Merck). For reaction monitoring, precoated silica gel 60 F254 TLC sheets (Merck) were used. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 UV/vis spectrophotometer. FT-IR spectra were recorded on a Perkin Elmer RXI spectrometer. High-resolution mass spectra (HRMS) were recorded using an LCT micro mass spectrometer. HPLC was performed using Shimadzu Prominence (LC 20 AT) liquid chromatography on a C_{18} column (4.5 mm × 250 mm) with a UV/vis detector. Photolysis of all the ester was carried out using 125 W medium pressure mercury lamp supplied by SAIC (India).

General procedure for the synthesis of carboxylates of (*E*)-1-acetylferrocene oxime

To the dry DCM solution of 1-acetylferroceneoxime (0.15 g, 0.61 mmol), acid chloride (0.73 mmol) and Et_3N (0.20 mL, 1.22 mmol) were slowly added at 0 °C. The reaction mixture was stirred for 12–15 h at room temperature. After the completion of the reaction (as indicated by TLC), it was quenched by ice cold water and diluted with DCM. The organic layer was separated and dried over Na_2SO_4, and the solvent was removed under vacuum to yield crude carboxylate.

(*E*)-1-[(Acryloxyimino)ethyl] ferrocene (3a). The dark red crude product on purification by column chromatography (5% ethyl acetate/hexane) resulted in the title compound **3a** (0.18 g, 82%) as a gummy solid; TLC R_f (20% ethyl acetate/hexane) 0.40; FTIR (neat) v_{max} (cm^{-1}): 1743, 1654; ^{1}H NMR (CDCl$_3$, 200 MHz) δ: 2.33 (s, 3H), 4.24 (s, 5H), 4.44–4.45 (m, 2H), 4.74–4.75 (m, 2H), 5.97 (d, 1H, J = 10.4 Hz), 6.25–6.38 (m, 1H), 6.60 (d, 1H, J = 10.4

Hz); ^{13}C NMR (CDCl$_3$, 50 MHz) δ: 14.8, 67.6 (2C) 69.5 (5C), 69.7 (2C), 78.6, 126.7, 131.4, 163.6, 164.9 HRMS (ES$^+$) calcd for C$_{15}$H$_{16}$FeNO$_2$ [M + H]$^+$ 298.0525, found 298.0538.

(E)-1-[(Benzoyloxyimino)ethyl] ferrocene (3b). The crude carboxylate was purified by column chromatography (5% ethyl acetate/hexane) to yield the title compound **3b** (0.17 g, 80%) as a brown solid, mp: 59–62 °C; TLC R_f (30% ethyl acetate/hexane) 0.45; FTIR (KBr) v_{max} (cm^{-1}): 1742, 1610; ^{1}H NMR (CDCl$_3$, 200 MHz) δ: 2.38 (s, 3H), 4.21 (m, 5H), 4.41 (m, 2H), 4.74 (m, 2H), 7.44–7.59 (m, 3H), 8.12 (d, 2H, J = 7.0 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 15.0, 67.7 (2C), 69.5 (5C), 70.6 (2C), 78.5, 128.4 (2C), 129.3, 129.4 (2C), 133.0, 163.6, 165.2; HRMS (ES$^+$) calcd for C$_{19}$H$_{18}$FeNO$_2$ [M + H]$^+$ 348.0681, found 348.0691.

(E)-1-[4-(Methyl-benzoyloxyimino)ethyl] ferrocene (3c). The crude product was purified by column chromatography (5% ethyl acetate/hexane) to yield the title compound **3c** (0.19 g, 84%) as a red solid, mp: 85–88 °C; TLC R_f (30% ethyl acetate/hexane) 0.45; FTIR (KBr) v_{max} (cm^{-1}): 1743, 1654; ^{1}H NMR (CDCl$_3$, 200 MHz) δ: 2.40 (s, 3H), 2.44 (s, 3H), 4.23 (m, 5H), 4.43–4.44 (m, 2H), 4.74–4.75 (m, 2H), 7.27–7.31 (m, 2H), 8.01 (d, 2H, J = 8.2 Hz); ^{13}C NMR (CDCl$_3$, 50 MHz) δ: 15.0, 22.6, 67.7 (2C), 69.4 (5C), 70.6 (2C), 78.7, 126.5, 129.1 (2C), 129.5 (2C), 143.8, 163.6, 165.8; HRMS (ES$^+$) calcd for C$_{20}$H$_{20}$FeNO$_2$ [M + H]$^+$ 362.0838, found 362.0846.

(E)-1-[4-(Methoxy-benzoyloxyimino)ethyl] ferrocene (3d). The orange solid compound **3d** (0.19 g, 85%) was obtained on purification of the crude product by column chromatography (4% ethyl acetate/hexane); mp: 104–106 °C; TLC R_f (20% ethyl acetate/hexane) 0.45; FTIR (KBr) v_{max} (cm^{-1}): 1743, 1610; ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 2.38 (s, 3H), 3.88 (s, 3H), 4.21 (m, 5H), 4.42 (m, 2H), 4.74 (m, 2H), 6.96 (d, 2H, J = 8.8 Hz), 8.07 (d, 2H, J = 8.8 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 14.9, 55.4, 67.0 (2C), 69.4 (5C), 70.5 (2C), 78.8, 113.7 (2C), 121.6, 131.5 (2C), 163.4, 163.5, 164.8; HRMS (ES$^+$) calcd for C$_{20}$H$_{20}$FeNO$_3$ [M + H]$^+$ 378.0787, found 378.0793.

General procedure for the synthesis of sulfonates of (E)-1-acetylferrocene oxime

To the mixture of sulfonyl chloride (0.74 mmol) and 1-acetylferroceneoxime (0.150 g, 0.61 mmol) in dry DCM, Et$_3$N (0.43 mL, 3.09 mmol) was added dropwise at 0 °C. The reaction mixture was then stirred overnight at room temperature. After the completion of the reaction (as indicated by TLC), it was quenched by ice cold water and diluted with DCM. The organic layer was separated and dried over Na$_2$SO$_4$, and the solvent was removed under vacuum to yield crude sulfonate.

(E)-1-[(Methanesulfonoxyimino)ethyl] ferrocene (4a). The crude product was purified by column chromatography (5% ethyl acetate/hexane) to yield the title compound **4a** (0.16 g, 80%) as a deep red solid, mp: 62–65 °C; TLC R_f (20% ethyl acetate/hexane) 0.50; FTIR (KBr) v_{max} (cm^{-1}): 1295, 1568; ^{1}H NMR (CDCl$_3$, 100 MHz) δ: 2.69 (s, 3H), 3.13 (s, 3H), 4.25 (m, 5H), 4.62 (m, 2H), 4.81 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 22.0, 43.2, 69.9 (2C), 70.5 (5C), 73.6 (2C), 80.4, 185.0; HRMS (ES$^+$) calcd for C$_{13}$H$_{16}$FeNO$_3$S [M + H]$^+$ 322.0195, found 322.0199.

(E)-1-[(Benzenesulfonoxyimino)ethyl] ferrocene (4b). The dark brown crude solid sulfonate on purification by column chromatography (50% ethyl acetate/hexane) gave title compound **4b** (0.19 g, 81%) as a deep brown colour gummy solid, mp: 120–125 °C; TLC R_f (25% ethyl acetate/hexane) 0.45; FTIR (KBr) v_{max} (cm^{-1}): 1292, 1546; ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 2.75 (m, 3H), 4.25 (m, 5H), 4.63–4.64 (m, 2H), 4.83–4.84 (m, 2H), 7.53–7.63 (m, 3H), 8.02–8.05 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 21.9, 70.2 (2C), 70.5 (5C), 73.8 (2C), 80.6, 126.9 (2C), 128.9 (2C), 132.5, 142.1, 185.5; HRMS (ES$^+$) calcd for C$_{18}$H$_{18}$FeNO$_3$S [M + H]$^+$ 384.0351, found 384.0365.

(E)-1-[(p-Styrenesulfonoyloxyimino)ethyl] ferrocene (4c). The crude product was purified by column chromatography (2% ethyl acetate/hexane) to yield the title compound **4c** (0.81 g, 80%) as a gummy solid; TLC R_f (20% ethyl acetate/hexane) 0.45; FTIR (KBr) v_{max} (cm^{-1}): 1298, 1517; ^{1}H NMR (CDCl$_3$, 200 MHz) δ: 2.73 (s, 3H), 4.21 (m, 5H), 4.61–4.63 (m, 2H), 4.80–4.82 (m, 2H), 5.42 (d, 1H, J = 10.8 Hz), 5.89 (d, 1H, J = 17.6 Hz), 6.70–6.84 (m, 1H), 7.55 (d, 2H, J = 8.4 Hz), 7.96 (d, 2H, J = 8.4 Hz); ^{13}C NMR (CDCl$_3$, 50 MHz) δ: 21.7, 69.5 (2C), 70.3 (5C), 73.6 (2C), 78.6, 116.9, 126.3 (2C), 127.1 (2C), 135.5, 140.9, 145.4, 181.0; HRMS (ES$^+$) calcd for C$_{20}$H$_{20}$FeNO$_3$S [M + H]$^+$, 410.0508 found 410.0515.

(E)-1-[(2,4-Difluorobenzenesulfonoxyimino)ethyl] ferrocene (4d). The dark brown crude product on purification by column chromatography (5% ethyl acetate/hexane) resulted the title compound **4d** (0.20 g, 78%) as a brown solid; TLC R_f (25% ethyl acetate/hexane) 0.40; mp: 135–140 °C; FTIR (KBr) v_{max} (cm^{-1}): 1298, 1517; ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 2.77 (s, 3H), 4.26 (m, 5H), 4.64–4.65 (m, 2H), 4.82–4.83 (m, 2H), 6.95–7.01 (m, 2H), 8.00–8.06 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 22.1, 69.5 (2C), 70.4 (5C), 73.9 (2C), 111.3, 118.7, 124.3, 130.7, 147.0, 164.4, 166.9, 186.0; HRMS (ES$^+$) calcd for C$_{18}$H$_{16}$F$_2$FeNO$_3$S [M + H]$^+$ 420.0163, found 420.0172.

Photogeneration of carboxylate acids and quantum yield measurement

A 0.039 mmol sample of carboxylate (**3a–d**) was dissolved in MeOH–H$_2$O (95 : 1) and individually irradiated by 125 W medium pressure Hg lamp using pyrex filter. The photoreaction was monitored by HPLC using methanol as mobile phase, at a flow rate of 1 mL min^{-1} (detection: UV 254 nm) at regular intervals of time. Peak areas were determined by HPLC, which indicated an increase in the acid concentration with time. Based on HPLC data for each compound, we plotted the logarithm of concentration of acid [ln C] versus irradiation time (t). We observed a linear correlation for the formation of the acids, which suggested a first order reaction and the corresponding rate constant was calculated. Further, the quantum yield for the photolysis of compound **3a–e** was calculated using eqn (1):

$$(\phi_p)_{PAG} = \frac{(k_p)_{PAG}}{I_0 (F_{PAG})} \qquad (1)$$

where Φ_p is the photolysis quantum yield, K_p is the photolysis rate constant, I_0 is the incident photon flux and F is the fraction of light absorbed. The quantum yield for the photogeneration of

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carboxylic acids was analyzed by employing valerophenone as an actinometer.

Preparative photolysis of carboxylate esters (3a–e)

A solution of carboxylate (3a–e) (0.27 mmol) in 120 mL of MeOH–H$_2$O (95 : 1) was individually irradiated by 125 W medium pressure Hg lamp using pyrex filter. The irradiation was monitored by TLC at regular intervals. After completion of photolysis, solvent was removed under reduced pressure, and the photoproducts 1-acetylferrocene and the corresponding carboxylic acids were isolated by column chromatography using EtOAc in hexane as an eluent.

Procedure for synthesis of caprolactone-based polymer (19)

One equivalent of the oxime was taken in round bottom flask and dissolved in 15 mL of dry toluene. Ten equivalents of ξ-caprolactone in 2 mL dry toluene were added to it at 80 °C for 10 min followed by the addition of 5 mol% tin octatate Sn(Oct)$_2$, and the post reaction mixture was heated at 100 °C temperature for 16 h. It was then cooled to room temperature and precipitated from cold hexane, and the precipitate was washed with ice cold hexane several times and dried under high vacuum.

Copolymer AFO-PCL (19). Red solid; FTIR (KBr) v_{max} (cm^{-1}): 1785; ^{1}H NMR (CDCl$_3$, 200 MHz) δ: 4.03 (brs), 3.61 (m), 2.29 (m), 1.62 (m), 1.38 (m).

Application of PAGs based on acetylferrocene in sol–gel transition

Samples were prepared by combining the CaCO$_3$ particles with a solution of sodium alginate and PAG in distilled water. Each mixture was stirred overnight by a magnetic stirring bar and was then sonicated using a Branson 1510 sonicator for 45 min at 40 kHz. Samples (2 mL) were placed in a 10 mL vial and irradiated with UV light ($\geq$365 nm) by 125 W medium pressure Hg lamp using a suitable filter (1 M CuSO$_4$ solution in 0.1 N H$_2$SO$_4$). During irradiation, the sample was stirred with a magnetic stirring bar.

Photopatterning. A given sample (50 mg) was smeared on a portion of a glass slide, and this region was then exposed to UV light ($\geq$365 nm) through a homemade photomask or stencil. After 45 min of UV exposure, the slide was rinsed with 1% NaCl to wash off the non-photolysed portions, thus revealing the photopatterned features.

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Notes and references

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