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Development of 1-Hydroxy-2(1*H*)-quinolone-Based Photoacid Generators and Photoresponsive Polymer Surfaces

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Abstract: A new class of carboxylate and sulfonate esters of 1-hydroxy-2(1H)-quinolone has been demonstrated as nonionic photoacid generators (PAGs). Irradiation of carboxylates and sulfonates of 1-hydroxy-2(1H)-quinolone by UV light ($\lambda \ge 310$ nm) resulted in homolysis of weak N–O bond leading to efficient generation of carboxylic and sulfonic acids, respectively. The mechanism for the homolytic N–O bond cleavage was supported by timedependent DFT calculations. Photoresponsive 1-(*p*-styrenesulfonyloxy)-2-quinolone–methyl methacrylate (SSQL-

Keywords: copolymerization • hydroxyquinolones • photoacid generators • photochemistry • thin films MMA) and 1-(*p*-styrenesulfonyloxy)-2quinolone–lauryl acrylate (SSQL-LA) copolymers were synthesized from PAG monomer 1-(*p*-styrenesulfonyloxy)-2-quinolone, and subsequently controlled surface wettability was demonstrated for the above-mentioned photoresponsive polymers.

Introduction

Photoacid generators (PAG) are among the critical formulation components that have long been used in the field of photoresists for semiconductor fabrication.^[1] On activation by external light source, PAGs generate acid which catalyzes important chemical transformations within the polymer film, such as deprotection, polymerization initiation, chain scission, and cross-linking.^[2] These processes either make the polymer more soluble in developing solvent, resulting in positive resists,^[3,4] or less soluble to generate negative resists.^[5,6] Recently, use of PAGs in tailoring smart photoresponsive polymers^[7] which change their wettability in response to external light stimulus has gained great attention, particularly in the field of microfluidics and lab-on-a-chip technologies.

To meet the demand of emerging applications in the microelectronics industry, various kinds of ionic^[8,9] and nonionic^[10,11] PAGs as well as binder polymers bearing an acidcleavable protecting group^[12] were synthesized. Among the nonionic PAGs, *N*-hydroxyamides,^[13] *N*-hydroxyimides,^[14] iminosulfonates^[15] and *N*-acyl-*N*-phenylhydroxylamines^[16] have attracted considerable attention, as they have a weak N–O bond which can be easily cleaved either by direct^[11] or sensitized^[17] photolysis. Our search of simple organic mole-

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cules which can act as efficient PAGs for both carboxylic and sulfonic acids by photoinduced homolytic N-O bond cleavage led us to explore 2-pyridone derivatives.

Facile N-O bond cleavage in 2-pyridone derivatives has been efficiently utilized for generation of carbon-,^[18] nitrogen-,^[19,20] and oxygen-centered^[21-23] radicals. Furrer observed that photolysis of 4,6-dimethylbenzyloxypyridone led to homolytic N-O bond cleavage with loss of benzaldehyde.[24] Katritzky and co-workers demonstrated that photolysis or thermolysis of N-acyloxy and N-benzoyloxy derivatives of 1hydroxy-4,6-diphenyl-2-pyridone undergo smooth N-O bond fission to produce rearranged 3- and 5-acyloxy and -benzoyloxy derivatives.^[25] Recently, irradiation of N-hydroxy-2-pyridone resulted in efficient generation of hydroxyl radicals, which in turn were shown to damage DNA effectively.^[26] Despite the widespread applications of 2-pyridone derivatives, so far their usage as PAGs has not been explored. Our interest in developing PAGs which can operate at $\lambda > 310$ nm, encouraged us to design 1-hydroxy-2(1H)-quinolone having a 1-hydroxy-2-pyridone nucleus as a PAG for carboxylic and sulfonic acids based on its N-O bond-cleavage chemistry.

Here we describe the synthesis and characterization of carboxylates and sulfonates of 1-hydroxy-2(1H)-quinolone as new PAGs, demonstrate photoacid generation, and discuss the mechanism of N–O bond cleavage. Furthermore, we constructed photoresponsive polymer using PAG monomer and demonstrated its application in creating photoresponsive surfaces with controlled wettability.

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Results and Discussion

Carboxylates of 1-hydroxy-2(1*H*)-quinolone as PAGs for carboxylic acids:

Synthesis of carboxylate esters of 1-hydroxy-2(1H)-quinolone: We synthesized carboxylate esters of 1-hydroxy-2(1H)quinolone 5a-e as shown in Scheme 1. Quinoline N-oxide (2) was prepared by treatment of quinoline with 30% H₂O₂



Scheme 1. Synthesis of carboxylates of 1-hydroxy-2(1*H*)-quinolone (5a-e).

in the presence of glacial acetic acid. Treatment of **2** with Pb(OAc)₄ in dry benzene resulted in formation of 2-hydroxyquinoline-1-oxide, which on tautomerization yielded stable 1-hydroxy-2(1*H*)-quinolone (**4**).^[27] Reaction of **4** with various acid chlorides in the presence of triethylamine in dry CH₂Cl₂ at 0 °C resulted in carboxylates of 1-hydroxy-2(1*H*)-quinolone^[28] in excellent yields (**5a–e**, Table 1). All carboxylates were characterized by ¹H and ¹³C NMR, IR, and mass spectral analysis.

Solvent effect on the photogeneration of carboxylic acid by *PAG* **5***b*: To identify the best solvent for effective generation of carboxylic acids from their corresponding PAGs, we carried out photolysis of **5***b* in MeOH, MeCN, THF, CHCl₃,

Table 1. Synthetic yield, UV/Vis, and photolysis data of carboxylate esters of 1-hydroxy-2(1H)-quinolone (**5a**-**e**).

	Synthetic	UV/Vis		Photogeneration of carboxylic acids			
	yield [%] ^[a]	λ ^[b]	lg $\varepsilon^{[c]}$	$t [\min]^{[d]}$	$\begin{array}{l} \text{Yield}^{[e]} \\ (\text{R}^{1}\text{CO}_{2}\text{H}) \end{array}$	$arPhi^{[\mathrm{f}]}$	
5a	89	325	3.15	40	90	0.090	
5 b ^[g]	90	331	3.79	35	90	0.101	
5 c ^[g]	92	330	3.75	25	95	0.152	
5 d ^[g]	85	332	3.85	22	97	0.177	
5 e ^[g]	80	334	3.90	50	85	0.068	

[a] Yield of isolated compound. [b] Maximum absorption wavelength. [c] Molar absorption coefficient. [d] Photolysis time. [e] Photolysis yield based on HPLC. [f] Quantum yield for the generation of various carboxylic acids at room temperature (error limit within $\pm 5\%$). [g] Carboxylates for which the photoproducts were isolated and compared with authentic samples.

benzene, MeCN: H_2O (50:1), and MeOH/ H_2O (50:1) for 35 min using a 125 W medium-pressure Hg lamp with Pyrex sleeve (Table 2).

Table 2.	Photolysis	of carb	oxylate	5b ir	n various	solvents
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Solvent	Acid [%] ^[a]	$arPhi^{[b]}$	
MeOH	75	0.086	
CAN	60	0.068	
THF	20	0.022	
CHCl ₃	40	0.047	
benzene	25	0.028	
MeCN:H ₂ O (50:1)	65	0.074	
MeOH/H ₂ O (50:1)	90	0.101	

[a] Photolysis yield based on HPLC. [b] Quantum yield for generation of benzoic acid at room temperature (error limit $\pm 5\%$).

In all of the above-mentioned solvents, carboxylate **5b** undergoes N–O bond homolysis to produce benzoic acid and quinolin-2(1*H*)-one. The highest quantum and chemical yields of benzoic acid were found in MeOH/H₂O (50:1). In weakly polar solvents such as THF and in nonpolar solvents like benzene, the photochemical yield of benzoic acid was relatively low, since several other minor photoproducts, which were not isolated, were formed.

Photolysis of carboxylate esters of 1-hydroxy-2(1H)-quinolone (5*a*-*e*): We photolyzed esters 5*a*-*e* in MeOH/H₂O (50:1) using a light source of $\lambda \ge 310$ nm (Scheme 2) and



Scheme 2. Photogeneration of carboxylic acids **7a-e** from their corresponding carboxylate esters **5a-e**.

found that the corresponding carboxylic acids were generated in nearly quantitative yield (Table 1). In each case the photolysis was stopped when conversion reached at least 95% (as indicated by HPLC). The photoproducts (carboxylic acid and quinolin-2(1*H*)-one) were isolated and characterized by comparison of ¹H NMR spectral data with those of corresponding authentic samples. Quantum yields for the generation of various carboxylic acids, determined by using valerophenone as an actinometer,^[29] were found to be in the range of 0.177 to 0.068.

For example, Figure 1 shows the HPLC of **5c** at regular interval of irradiation. Depletion of the peak at elution volume $V_e = 44.6 \text{ mL}$ with increasing irradiation time indicates photodecomposition of carboxylate **5c**, while two new major peaks around $V_e = 5$ and 20.5 mL, corresponding to the major photoproducts *p*-toluic acid (**7c**) and quinolin-2(1*H*)-one (**6**), respectively, gradually increased. Photoproducts **7c** and **6** were identified by co-injection with their corresponding authentic samples.

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Figure 1. HPLC data of photolysis of ester 5c at regular time intervals. a) 0, b) 5, c) 10, d) 25 min. UV absorption at 254 nm.

Among different carboxylates, **5d** having an electron-donating methoxyl substituent on the aromatic carboxylic moiety generated carboxylic acid with higher quantum yield than carboxylate **5e** with electron-withdrawing nitro substituent.

Sulfonates of 1-hydroxy-2(1*H*)-quinolone as PAGs for sulfonic acids

Synthesis of sulfonates of 1-hydroxy-2(1H)-quinolone: Synthesis of sulfonates of 1-hydroxy-2(1H)-quinolone **8a–e** is outlined in Scheme 3. Treatment of 1-hydroxy-2(1H)-quinolone (**4**) with various sulfonyl chlorides in presence of Et₃N in dry CH₂Cl₂ at 0°C resulted in sulfonate esters of 1-hy-



Scheme 3. Synthesis of sulfonates of 1-hydroxy-2(1*H*)-quinolone (8a–e). X-ray crystal structure of sulfonate ester 8c (reference [30]).

droxy-2(1*H*)-quinolone 8a-e in good yields (Table 3). All of the sulfonate esters were characterized by ¹H and ¹³C NMR, IR, and mass spectral analysis. The structure of 8c was confirmed by XRD analysis (Scheme 3).

Table 3. Synthetic yield, UV/Vis, and photolysis data of sulfonate esters of 1-hydroxy-2(1H)-quinolone (**8a–e**).

	Synthetic yield [%] ^[a]	UV $\lambda^{[b]}$	V/V is $\lg \varepsilon^{[c]}$	Photogeneration of sulfonic ac $t [min]^{[d]}$ Yield^{[e]} $\Phi^{[}$ (R^2SO_3H)		
8a	90	329	3.58	25	90	0.144
8b	88	328	3.70	30	90	0.120
8 c	93	329	3.83	20	95	0.190
8 d	90	330	3.98	20	97	0.194
8 e	85	332	3.81	35	85	0.097

[a] Yield of isolated compound. [b] Maximum absorption wavelength. [c] Molar absorption coefficient. [d] Photolysis time. [e] Photolysis yield based on ¹H NMR spectroscopy. [f] Quantum yield for the generation of various sulfonic acids at room temperature (error limit $\pm 5\%$).

Photolysis of sulfonate esters 8a-e for generation of sulfonic acids: Irradiation of aqueous methanolic solutions (50:1) of sulfonates 8a-e by a procedure similar to the generation of carboxylic acids (see above) resulted in efficient N–O bond cleavage to generate the corresponding sulfonic acids in high yields (Scheme 4, Table 3). Photolysis was monitored by ¹H NMR spectroscopy and the reaction was stopped when the conversion reached about 90%. In all cases, we obtained sulfonic acids 9a-e as significant photoproducts along with quinolin-2(1*H*)-one (6).



Scheme 4. Photogeneration of sulfonic acids **9a–e** from their corresponding sulfonate esters **8a–e**.

For example, Figure 2 shows ¹H NMR spectra of sulfonate **8a** in CDCl₃ at regular intervals of irradiation. Decreasing intensity of the signal at 3.71 ppm for the methyl group with irradiation time indicates photodecomposition of **8a**, while a signal at 3.01 ppm corresponding to the methyl group of methanesulfonic acid gradually increased. In addition, gradual appearance of a broad singlet at 15.14 ppm for an OH proton, which disappeared on D₂O exchange, confirmed formation of sulfonic acid. Furthermore, generation of sulfonic acids from their corresponding sulfonates **8a–e** was studied by monitoring the pH change^[31] of the photolysate (2×10^{-4} M) at regular intervals of irradiation (Figure 3).

Mechanism for photogeneration of carboxylic and sulfonic acids: On the basis of the mechanistic studies by Sakurai and co-workers on the photolysis of l-(benzoyloxy)-2-pyri-

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Figure 2. H NMR spectra of sulfonate **8a** at regular intervals of irradiation in CDCl₃.



Figure 3. Comparison of pH change on photolysis of different sulfonates $(2 \times 10^{-4} \text{ M}, 8 \text{ a-d})$ at regular intervals of irradiation in MeOH/H₂O (50:1).

done^[32] and by Malval et al. on the photolysis of perfluorinated naphthalimides,^[11] as well as our solvent study, we suggest that both carboxylates **5a–e** and sulfonates **8a–e** of 1hydroxy-2(1*H*)-quinolone undergo homolytic N–O bond cleavage from the singlet excited state to generate 1-quinolinyl and acyloxy or sulfonyl radical pairs (Scheme 5). In aqueous polar protic solvent, the radical pair escapes from the cage and subsequently abstracts a hydrogen atom from the solvent to produce the corresponding carboxylic or sulfonic acid (**7a–e** or **9a–e**) and quinolin-2(1*H*)-one (**6**), which was confirmed by XRD analysis (Scheme 5).

A photoinduced homolytic N–O bond cleavage mechanism was further supported by time-dependent DFT (B3LYP-D/def2-SVP) calculations (see Experimental Section and Supporting Information Figure S3 for details).



Scheme 5. Mechanism for photogeneration of carboxylic and sulfonic acids from PAGs. X-ray crystal structure of photoproduct quinolin-2(1H)-one (6, reference [33]).

Polymers derived from 1-(*p*-styrenesulfonyloxy)-2-quinolone as sulfonic acid generators: After successfully demonstrating sulfonates of 1-hydroxy-2(1H)-quinolone as PAGs for sulfonic acids, we focused on the synthesis of polymers bearing sulfonates of 1-hydroxy-2(1H)-quinolone which can act as PAGs for sulfonic acids, since they can be useful for the development of photoresponsive surfaces.

Synthesis of 1-(*p*-styrenesulfonyloxy)-2-quinolone (SSQL) monomer: The monomer 1-(*p*-styrenesulfonyloxy)-2-quinolone (**11**) was synthesized by treating *p*-styrenesulfonyl chloride^[34] (**10**) with 1-hydroxy-2(1*H*)-quinolone (**4**) in the presence of Et₃N in dry CH₂Cl₂ under nitrogen atmosphere (Scheme 6).



Scheme 6. Synthesis of monomer 1-(*p*-styrenesulfonyloxy)-2-quinolone (11).

Synthesis of 1-(p-styrenesulfonyloxy)-2-quinolone-methyl methacrylate (SSQL-MMA) and 1-(p-styrenesulfonyloxy)-2quinolone-lauryl acrylate (SSQL-LA) copolymers: Polymerization was carried out by a free-radical method with 2,2'azobisisobutyronitrile (AIBN) as initiator.^[35] The monomers 1-(p-styrenesulfonyloxy)-2-quinolone (**11**) and methyl methacrylate (MMA, **12**) were dissolved in THF and AIBN was added (molar monomer:AIBN ratio 200:1) under nitrogen atmosphere. The reaction mixture was heated at 80 °C for 3 h to yield the corresponding polymer SSQL-MMA (**14**). For the synthesis of polymer SSQL-LA (**15**) the above procedure was adopted, except that lauryl acrylate (LA, **13**) was used instead of methyl methacrylate (Scheme 7).



Scheme 7. Synthesis of copolymers SSQL-MMA (14) and SSQL-LA (15).

Characterization of polymers SSQL-MMA (14) and SSQL-LA (15):

Molecular weights and polydispersity of polymers SSQL-MMA (14) and SSQL-LA (15) were recorded by gel permeation chromatography (GPC); the results are tabulated in Supporting Information Table S1. GPC (Figure 4) was car-



Figure 4. GPC of random copolymers SSQL-MMA (14) and SSQL-LA (15) and homopolymer of SSQL (16).

ried out at ambient temperature by using a Viscotek-GPC system equipped with two GMH HR-H Non Polar organic columns in series. DMF was used as eluent at a flow rate of 1 mLmin⁻¹. Polystyrene standards in the M_n range of 2000–395000 were used for calibration. The polymers were also characterized by UV, IR, and ¹H NMR spectroscopy.

Photogeneration of sulfonic acid from polymers SSQL-MMA (14) and SSQL-LA (15): To investigate the polymers as PAGs, the SSQL-MMA (14) was spin-coated onto glass wafers by using a Headway Research spinner (Spin Coating Unit SCU 2005). The polymer films were then baked at



Scheme 8. Photogeneration of sulfonic acid on irradiation of a polymer thin film.

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90 °C for 5 min in an oven. The film thicknesses were measured with a DekTak-150 film thickness measurement gauge and were in the range of 0.5–0.8 µm. Irradiation of the polymer thin films ($\lambda \ge 310$ nm) with a medium-pressure Hg lamp (incident photon flux I_0 -($\lambda \ge 310$ nm)=1.25 ×

 10^{17} photon s⁻¹ cm⁻²) at room temperature in air resulted in

homolytic N–O bond cleavage followed by hydrogen abstraction from the residual solvent in the film or polymer molecule leading to the generation of sulfonic acids (Scheme 8).

The FTIR spectra (see Supporting Information Figure S1) indicated photodecomposition of SSQL-MMA films on irradiation at $\lambda \ge 310$ nm. The peaks at 1387, 1193, and 1180 cm⁻¹ (vSO₂) due to the aminosulfonate group decrease on irradiation, which indicates the photodecomposition of the polymer. Generation of sulfonic acid by the polymer films was confirmed by the acid-catalyzed polysiloxane formation technique.^[36] FTIR spectra (Supporting Information Figure S2) showed changes to the irradiated film before and after treatment with methyltriethoxysilane (MTEOS). The appearance of new peaks at 780 (SiCH₃), 900 (SiOH), 1000–1200 (SiOSi), and 3200–3500 cm⁻¹ (SiOH) for the irradiated film indicates formation of silanol, obtained on hydrolysis of MTEOS under humid conditions by the newly generated polymer containing sulfonic acid.

Investigation of tunable surface properties: To investigate the photoresponsive surface^[7] properties of our designed polymer, we spin-coated and made a smooth-surfaced polymer film on a glass slide using copolymer SSQL-LA. Initially the surface was hydrophobic in nature and showed large contact angle (CA \approx 130°). Roughness and trapped air^[37] are the factors responsible for the observed hydrophobicity of the polymer, but the polymer film loses its hydrophobicity and becomes hydrophilic on direct UV light irradiation ($\lambda \geq$ 310 nm). On photolysis the polymer generates polar SO₃H groups which cover the surface of the film. Due to the strong affinity of SO₃H groups towards water molecules, the CA decreases,^[38] as shown in Figure 5.

The irreversible hydrophobicity/hydrophilicity is controlled by irradiation time. Increase of irradiation time results in generation of more SO_3H groups on the surface, which



Figure 5. Water drop on polymer film a) before and b) after photoirradiation.

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Figure 6. Variation of contact angle of **SSQL-LA** polymer film with irradiation time.

lead to decreases in contact angle. The change from hydrophobicity to hydrophilicity in terms of contact angle is shown in Figure 6.

Conclusion

We have developed for the first time carboxylates and sulfonates of 1-hydroxy-2(1H)-quinolone as PAGs based on their facile N-O bond cleavage. Carboxylates and sulfonates of 1hydroxy-2(1H)-quinolone were prepared by simple synthetic procedures in high yields. In particular, sulfonates of 1-hydroxy-2(1H)-quinolone were found to be stable at room temperature, in contrast to our earlier sulfonates of Nacetyl-N-phenylhydroxylamines,^[10] which efficiently rearranged to form O-arenesulfonates. Irradiation of carboxylates and sulfonates of 1-hydroxy-2(1H)-quinolone in aqueous methanol ($\lambda \ge 310$ nm) generated the corresponding carboxylic and sulfonic acids in good quantum yields. Density functional calculations showed that homolytic N-O bond cleavage takes place via the singlet excited state. The quantum yield for the generation of acids was found to be dependent on the solvent. Moreover, we have prepared a photoresponsive polymer surface using the copolymer SSQL-LA, and shown switchable wettability behavior of the polymer surface with large change in contact angle from hydrophobic to hydrophilic.

Experimental Section

General: ¹H NMR (200 MHz) spectra were recorded on a Bruker AC 200 spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 7.26 ppm) and coupling constants in Hz. ¹³C NMR spectra were recorded on a Bruker AC 200 spectrometer with complete proton decoupling. Chemical shifts are reported in ppm relative to tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 77.0 ppm). Chromatographic purification was done with 60– 120 mesh silica gel (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. FTIR spectra were recorded on a PerkinElmer RXI spectrometer. High-resolution mass spectra (HRMS) were recorded on an LCT micro mass spectrometer. HPLC was performed with a Shimadzu Prominence (LC 20 AT) liquid chromatograph on a C_{18} column (4.5×250 mm) with a UV/Vis detector and hexane/propan-2-ol (9:1) as mobile phase. GPC was carried out at ambient temperature by using a Vistek GPC system equipped with two GMH HR-H Non Polar organic columns in series. Photolysis of all esters was carried out with a 125 W medium-pressure mercury lamp supplied by SAIC (India).

Computational methods: We performed DFT calculations using BP86^[39] and B3LYP^[40] functionals with empirical dispersion correction (DFT-D)^[41] in conjunction with def2-SVP^[42] basis set. Resolution of the identity (RI) approximations was used in BP86 calculations for speedup. Turbomole v6.2^[43] were used for all calculations. For excited-state calculations time-dependent DFT was employed. Unrestricted formalism was used. We included four lowest roots for each calculation. Dl-find,^[44] implemented in ChemShell,^[45] was used for optimizations. To compute transition states at the excited-state potential-energy surface (PES), the dimer method^[46] was used. Vibrational analysis was done using finite-difference Hessian in ChemShell for excited-state calculations and analytic gradients from Turbomole for ground-state calculations.

General procedure for the synthesis of carboxylates of 1-hydroxyquinoline-2(1*H*)-one (5a-e): Et₃N (0.43 mL, 3.09 mmol) was added dropwise to a mixture of acid chloride (1.86 mmol) and 1-hydroxy-2(1*H*)-quinolone (250 mg, 1.55 mmol) dry CH₂Cl₂ at 0 °C. The reaction mixture was stirred for 12 h at room temperature. After completion of the reaction (as indicated by TLC), it was quenched with ice-cold water and diluted with CH₂Cl₂. The organic layer was separated, dried over Na₂SO₄, and the solvent removed under vacuum to yield crude carboxylate.

1-(Napthylpropanoyloxy)-2-quinolone (5a): The crude carboxylate was purified by column chromatography (20% ethyl acetate/hexane) to give **5a** (89%) as a brown liquid; $R_{\rm f}$ (30% ethyl acetate/hexane) 0.45; FTIR (neat): $\tilde{\nu}_{\rm max} = 1648$, 1793 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): $\delta = 3.23$ (d, 2H, J = 6.0 Hz), 3.32 (d, 2H, J = 6.4 Hz), 6.46 (d, 1 H, J = 8.4 Hz), 6.74 (d, 1 H, J = 9.6 Hz), 6.88 (t, 1 H, J = 7.6 Hz), 7.11 (t, 1 H, J = 7.6 Hz), 7.42–7.54 (m, 4H), 7.66–7.77 (m, 2H), 7.79–7.82 (m, 1H), 7.85 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): $\delta = 31.1$, 33.4, 111.1, 119.7, 121.9, 123.1, 125.9, 126.4, 127.0, 127.2, 127.8, 127.9, 128.3, 128.7, 131.1, 132.5, 133.8, 137.0, 139.4, 150.0, 156.6, 168.9; HRMS (ES⁺) calcd for C₂₂H₁₇NO₃ [*M*+H⁺]: 343.1208, found: 343.1202.

1-(Benzoyloxy)-2-quinolone (**5b**):^[47] The dark yellow crude product was purified by column chromatography (20% ethyl acetate/hexane) to give **5b** (90%) as a pale yellow solid; $R_{\rm f}$ (30% ethyl acetate/hexane) 0.50; m.p. 120–122 °C; FTIR (KBr) $\tilde{\nu}_{\rm max}$ =1770, 1666 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): δ =6.81 (d, 1H, *J*=9.6 Hz), 7.21–7.39 (m, 2H), 7.43–7.58 (m, 4H), 7.59–7.64 (m, 1H), 7.67–7.78 (m, 1H), 8.28 (d, 2H, *J*=7.0 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ =111.1, 119.8, 121.9, 123.2, 125.9, 128.3, 128.5, 128.9, 130.0, 130.5, 131.2, 134.8, 138.5, 139.3, 156.8, 162.6; MS *m/z*: 305 (19%), 304 (80%, [*M*+Na⁺]), 282 (100%, [*M*+H⁺]), 214 (35%); HRMS (ES⁺) calcd for C₁₆H₁₁NO₃ [*M*+H⁺]: 265.0738, found: 265.0731.

1-(*p***-Methoxybenzoyloxy)-2-quinolone (5d)**: Compound **5d** (85%) was obtained as a pale yellow solid by purification of the crude product by column chromatography (40% ethyl acetate/hexane); R_f (30% ethyl acetate/hexane) 0.35; m.p. 145–147°C; FTIR (KBr) $\tilde{\nu}_{max} = 1692$, 1750 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): $\delta = 3.94$ (s, 3H), 6.86 (d, 1H, J = 9.6 Hz), 7.06 (d, 2H, J = 8.8), 7.26–7.38 (m, 2H), 7.49–7.56 (m, 1H), 7.61–7.69 (m, 1H), 7.81 (d, 1H, J = 9.6 Hz), 8.28 (d, 1H, J = 8.8 Hz); ¹³C NMR (CDCl₃, 50 MHz): $\delta = 55.8$, 111.4, 114.4, 115.5, 117.9, 120.0, 121.9, 122.8, 123.4, 128.6, 129.5, 131.4, 133.0, 138.6, 139.5, 157.2, 162.4; HRMS (ES⁺) calcd for C₁₇H₁₄NO₄ [*M*+H⁺]: 296.0917, found: 296.0913.

Photogeneration of carboxylic acids and quantum yield measurement: Carboxylate **5a–e** (0.05 mmol) was dissolved in MeOH/H₂O (50:1) and irradiated with a 125 W medium-pressure Hg lamp with Pyrex filter. In each case photolysis was stopped when conversion reached at least 90% (as indicated by HPLC). After completion of the photolysis, the solvent was removed under vacuum and the photoproducts (carboxylic acids and

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quinolin-2(1H)-one) were separated by column chromatography with ethyl acetate/hexane as eluent.

Quinolin-2(1*H***)-one (6)**: White solid; $R_{\rm f}$ (30% ethyl acetate/hexane) 0.50 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): δ =6.70 (d, 1H, J=9.4 Hz), 7.25–7.36 (m, 2H), 7.48–7.59 (m, 2H), 7.81 (m, 1H, J=9.6 Hz) 11.39 (brs, 1H), ¹³C NMR (CDCl₃, 100 MHz): δ =116.0, 119.2, 121.6, 123.0, 129.3, 130.9, 138.7, 141.2, 164.4.

The quantum yield for the photogeneration of carboxylic acids was analyzed by employing valerophenone as an actinometer. The progress of the photolysis was monitored by taking 5 μL of aliquot at regular time intervals and analyzing by HPLC with hexane/propan-2-ol (9:1) as eluent at a flow rate of 1 mLmin⁻¹ (detection: UV 254 nm). The percentage of carboxylic acid generated was determined by calculating the gradual increase in the peak area of the carboxylic acid.

General procedure for the synthesis of sulfonates of 1-hydroxy-2(1*H*)quinolone (8a–e): Et₃N (0.43 mL, 3.09 mmol) was added dropwise to a mixture of sulfonyl chloride (2.33 mmol) and 1-hydroxy-2(1*H*)-quinolone (250 mg, 1.55 mmol) in dry CH₂Cl₂ at 0 °C. The reaction mixture was then stirred overnight at room temperature. After completion of the reaction (as indicated by TLC), it was quenched with ice-cold water and diluted with CH₂Cl₂. The organic layer was separated, dried over Na₂SO₄, and the solvent removed under vacuum to yield crude sulfonate.

1-(Methanesulfonyloxy)-2-quinolone (8a): The dark yellow crude solid sulfonate was purified by column chromatography (30% ethyl acetate/ hexane) to give **8a** (90%) as a yellow solid; R_f (30% ethyl acetate/ hexane) 0.55; m.p. 108–110°C; FTIR (KBr): $\tilde{\nu}_{max} = 1683$, 1350 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): $\delta = 3.78$ (brs, 3H), 6.79 (d, 1H, J = 9.6 Hz), 7.33–7.41 (m, 1H), 7.64 (s, 1H), 7.68–7.69 (m, 1H), 7.24 (brs, 1H), 7.73–7.82 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz): $\delta = 41.9$, 121.6, 119.7, 127.4, 123.8, 128.3, 131.7, 139.4, 140.0, 157.4; HRMS (ES⁺) calcd for C₁₀H₉NO₄S [*M*+H⁺]: 239.0252, found: 239.0248.

1-(Benzenesulfonyloxy)-2-quinolone (8c): The crude product was purified by column chromatography (30% ethyl acetate/hexane) to give **8c** (93%) as an off-white solid; m.p.: 118–122 °C; $R_{\rm f}$ (30% ethyl acetate/hexane) 0.40; FTIR (KBr) $\tilde{\nu}_{\rm max}$ =1685, 1378 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): δ =6.64 (d, 2H, J=9.4 Hz), 7.30–7.34 (m, 1H), 7.58–7.67 (m, 5H), 7.72–7.81 (m, 2H), 8.17 (d, 2H, J=7.2 Hz); ¹³C NMR (CDCl₃, 50 MHz): δ =122.9, 119.8, 121.7, 123.7, 123.9, 128.2, 129.1 (2C), 129.8 (2C), 131.5, 135.2, 135.3, 139.7, 157.0; HRMS (ES⁺) calcd for C₁₅H₁₁NO₄S [*M*+H⁺]: 301.0408, found: 301.0411.

1-(*p***-Methylbenzenesulfonyloxy)-2-quinolone (8d):**^[48] Purification of the crude mixture by column chromatography (20% ethyl acetate/hexane) gave **8d** as an off-white solid; m.p. 121–124 °C; $R_{\rm f}$ (30% ethyl acetate/hexane) 0.45; FTIR (KBr): $\tilde{\nu}_{\rm max}$ =1378, 1678 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ =2.49 (s, 3H), 6.64 (d, 1H, J =9.6 Hz), 7.29–7.33 (m, 1H), 7.39–7.43 (m, 2H), 7.56–7.60 (m, 2H), 7.66–7.76 (m, 3H), 8.04 (d, 2H, J =9.4 Hz), 8.35–8.40 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ =21.8, 112.9, 119.7, 121.6, 123.5, 128.1, 129.6, 129.7 (2 C), 131.2, 131.5, 132.1, 134.0, 139.3, 146.2, 164.9; HRMS (ES⁺) calcd for C₁₆H₁₃NO₄S [*M*+H⁺]: 315.0565, found: 315.0568.

1-(*o***-Nitrobenzenesulfonyloxy)-2-quinolone (8e)**: Compound **8e** (80%) was obtained as a yellow solid by purification of the crude product by column chromatography (50% ethyl acetate/hexane); $R_{\rm f}$ (30% ethyl acetate/hexane) 0.35; m.p: 133–135°C; FTIR (KBr): $\tilde{\nu}_{\rm max} = 1668$, 1363 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): $\delta = 6.54$ (d, 1H, J = 9.6 Hz), 7.02–7.29 (m, 2H), 7.48–7.57 (m, 1H), 7.67 (d, 1H, J = 7.2 Hz), 7.85–7.96 (m, 2H), 8.07–8.21 (m, 3H); ¹³C NMR (CDCl₃, 50 MHz): $\delta = 122.02$, 122.3, 122.9, 123.6, 125.9, 126.9, 128.2, 132.0, 133.0, 133.6, 134.7, 137.8, 140.1, 148.6, 162.0; HRMS (ES⁺) calcd for C₁₅H₁₀N₂O₆S [*M*+H⁺]: 346.0259, found: 346.0251.

Photolysis and quantum yield measurements of the sulfonate esters: 0.05 mmol of sulfonate ester (8a–e) was dissolved in MeOH/H₂O (50:1) and irradiated by a 125 W medium-pressure Hg lamp with Pyrex filter. The progress of the reaction was monitored by ¹H NMR analysis. After completion of the reaction the solvent was removed under vacuum and the photo products (sulfonic acid and quinolin-2(1*H*)-one) were separated by column chromatography with ethyl acetate/hexane as an eluant.

The quantum yields for photogeneration of sulfonic acids were analyzed by ¹H NMR spectroscopy by employing valerophenone as an actinometer. The percentage of acid generated was determined by calculating the gradual increase in the peak area of the sulfonic acids with anisole as an internal standard by ¹H NMR.

Synthesis of monomer 1-(p-styrenesulfonyloxy)-2-quinolone (SSQL, 11): Et₃N (3.68 mL, 26.48 mmol) was added to a mixture of 1-hydroxy-2(1H)quinolone (2 g, 13.24 mmol) and p-styrenesulfonyl chloride (4 g, 19.73 mmol) in dry CH₂Cl₂ over 5 min at 0°C, and then the reaction mixture was continuously stirred at room temperature overnight. After completion of the reaction it was quenched with ice-cold water and diluted with CH2Cl2. The organic layer was separated, dried over Na2SO4, and the solvent removed under vacuum. The dark yellow crude solid was purified by column chromatography (40% ethyl acetate/hexane) to give 11 (85%) as a light yellow solid; $R_{\rm f}$ (40% ethyl acetate/hexane) 0.50; m.p. 105–107°C; FTIR (KBr): $\tilde{\nu}_{max} = 1650$, 1363 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): $\delta = 5.50$ (d, 1 H, J = 10.8 Hz), 5.94 (d, 1 H, J = 17.4 Hz), 6.64 (d, 1 H, J = 9.6 Hz), 6.79 (dd, 1 H, $J_1 = 10.8$ Hz, $J_2 = 17.6$ Hz), 7.29–7.32 (m, 1 H), 7.56–7.76 (m, 6 H), 8.11 (d, 2 H, J=8.4 Hz); ¹³C NMR (CDCl₃, 50 MHz): $\delta = 112.9$, 118.8, 119.8, 121.7, 123.6, 124.3, 126.7 (2 C), 128.2, 130.0 (2 C), 131.4, 133.7, 135.2, 139.7, 144.4, 157.0.

General procedure for synthesis of copolymers 14 and 15: SSQL monomer (1.526 mmol) and LA or MMA (1.526 mmol) were mixed in a 10 mL glass tube and dissolved by adding dry THF. AIBN (0.009 mmol) was added and the tube was then purged with nitrogen for 30 min. The reaction mixture was heated at 80° C for 3 h. After completion of the reaction the tube was immersed in liquid nitrogen and the reaction mixture diluted with THF. Polymer was then precipitated from hexane and the process was repeated three times to remove unconverted monomer and AIBN. It was then dried under high vacuum for 6 h.

Polymer SSQL-LA (14): Off-white liquid; UV/Vis (MeOH): $\lambda_{max} = 330 \text{ nm}$, FTIR (neat): $\tilde{\nu}_{max} = 1650$, 1355 cm^{-1} ; ¹H NMR (CDCl₃, 200 MHz): $\delta = 0.68-0.96$ (m), 1.02-2.18 (m), 2.12-2.54 (m), 3.55-4.46 (m), 6.66-7.50 (m), 7.55-8.12 (m).

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FULL PAPER



Facile N-O cleavage of carboxylate and sulfonate esters of 1-hydroxy-2(1H)-quinolone by UV light $(\lambda \ge 310 \text{ nm})$ has been exploited for use as nonionic photoacid generators (PAGs) for efficient generation of carboxylic and sulfonic acids, respectively.

Furthermore, photoresponsive copolymers were constructed from a styrylsubstituted PAG monomer and acrylate comonomers, and their light-controlled surface wettability was demonstrated (see figure).

Photoacid Generators -

M. Ikbal, R. Banerjee, S. Atta, A. Jana, D. Dhara,* A. Anoop,*

Development of 1-Hydroxy-2(1H)quinolone-Based Photoacid Generators and Photoresponsive Polymer Surfaces

