Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Materials Advances

Pourbaix Sensors in Polyurethane Molecular Logic-Based Coatings for Early Detection of Corrosion

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Chemicals

4-(2-Aminoethyl)morpholine (98%, Aldrich), *N,N*-dimethylethylenediamine (≥ 98.0%, Sigma-Aldrich), ferrocenecarboxaldehyde (98%, Acros), hydroxylamine (50 wt% in H_2O, Sigma-Aldrich), lithium aluminium hydride (97%, Alfa Aesar), methanesulfonic acid (≥ 99.5%, Sigma-Aldrich), perylene-3,4,9,10-tetracarboxylic dianhydride (97%, Sigma-Aldrich), quinoline (98%, Sigma-Aldrich), zinc acetate (analytical grade, Fisher Scientific), chloroform (HPLC grade, Sigma-Aldrich), tetrahydrofuran (HPLC grade, Sigma-Aldrich), methanol (HPLC grade, Sigma-Aldrich), dichloromethane (HPLC grade, Fisher Scientific), hexanes 40-60 °C (≥ 95%, mixture of isomers, Sigma Aldrich), petroleum ether (AR, bp 60-80 °C, Fisher), *N,N*-dimethylformamide (HPLC grade, Sigma-Aldrich), hydrochloric acid (37% w/w, Fisher) and 1,4-dioxane (99%, Sigma-Aldrich) were used as received. Silica gel 60 (70-230 mesh, Fluka Analytical) and (extra pure, low iron, 40-100 mesh, Fisher Chemical) were used for column chromatography (type WN 3, Aldrich). Silica gel on aluminium foil (with fluorescent indicator 254 nm, Fluka analytical) were used for thin-layer chromatography (TLC). 4Å molecular cylinder sieves (Aldrich) were dried in a furnace at 330 °C for 48 hours before use and stored in an oven at ~100°C.

Instrumentation

Melting points were measured using a Stuart SMP40 automatic melting point apparatus. Fourier transform infrared (FTIR) spectra were recorded using a Shimadzu IR–Affinity-1 spectrophotometer. Nuclear Magnetic Resonance (NMR) spectra were recorded with a Bruker Avance III HD NMR equipped with an Ascend 500 11.75 Tesla superconducting magnet and 5 mm PABBO probe at operating frequencies of 500.13 MHz. for ^1H nuclei, respectively. Spectra were processed with TOPSPIN® V3.5pl7 software. Chemical shifts were calibrated against tetramethylsilane (TMS) ($\delta = 0.00$ ppm). UV-visible absorption spectra were recorded on a Jasco V650 spectrophotometer connected to a PC running Windows XP and the spectra analysed with Spectra Manager Suite.® The instrumentation parameters were set to medium response, a bandwidth of 1.0 nm and a scan speed of 200 nm min^{-1}. Fluorescence measurements were recorded with a Jasco FP-8300 spectrofluorimeter analysed with Spectra Manager Suite®. The instrument parameters were set at 2.5 nm for both the excitation and emission slits, respectively. The scan rate was set at 200 cm^{-1}. Spectra were background subtracted for solvent. Quartz SUPRASIL cuvettes (101-10-40) with 10 mm pathlength with transparent windows on all four sides were used. pH/mV measurements were taken using a ProMinent® GmbH DULCOTEST® Portable handheld meter coupled to parallel temperature sensing. The temperature probe was an in-house modified pt 1000 sensor attached to the handheld meter by a coaxial cable and SN6 standard plugs calibrated with Merck® pH standards at pH 7.0 and pH 4.0. The pH sensor was a pH-reference combination probe from ProMinent® GmbH PHES 112 SE® double junction sensor. Redox readings in mV were taken using a Redox-Combination Probe from ProMinent® GmbH RHER-Pt-SE®. HRMS was performed by Medac Ltd UK.

Synthesis

Reactions were carried out in 50 mL or 100 mL round-bottomed flasks connected to Liebig condensers with ground glass joints and heated in a mineral oil bath on an IKA C-MAG HS 7 hotplate fitted with an IKA ETS-D5 temperature probe. For temperatures above 120 °C silica oil was used. Solvent removal was performed using a Stuart rotary evaporator with a temperature water bath and low pressure vacuum pump with vapour traps. Trace solvent was removed using an electric Roots vacuum pump and glass manifold by freeze drying with dry ice and subsequent slow heating under high vacuum. Reactions were monitored by TLC using Sigma-Aldrich® TLC plates 60 with fluorescent indicator visualised with a handheld lamp using 254 nm and 365 nm UV light. Logic gates **1** and **2** were synthesised according to literature procedures with slight modifications[S1] as shown in Scheme S1.

Synthesis of **1**, 2-(ferrocenylmethyl)-9-(2-(dimethylamino)ethyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone

In a 50 ml round-bottom flask intermediate **3** (0.60 g, 1.0 mmol) and ferrocenylmethyl amine (0.40 g, 1.8 mmol) were dissolved in 10 ml of quinoline and zinc acetate (0.10 g, 0.60 mmol) and heated at 160 °C for 4 hours. The cooled reaction was filtered through a fine glass sinter funnel under light vacuum and the product washed with cold DMSO (3×20 ml). A fine dark red powder was obtained by centrifugation in 35% yield (230 mg). R_f = 0.15 (DMSO); m.p. > 300 °C; ^{1}H NMR (DMSO-d_6, ppm, 30 °C): δ_H 8.86-8.56 (m, 8H, Ar-H), 5.05 (s, 2H, Fc-CH_2-N), 4.10-4.38 (m, 9H, Cp), 3.53-2.08 (m, 10H, $NCH_2CH_2N(CH_3)_2$); IR (KBr, cm^{-1}): 3065, 2945, 1701, 1696, 1692, 1663, 1654, 1605, 1497, 1466, 1648, 1350, 1214, 1021, 1055, 745, 793; HRMS (ES-ToF, m/z): calculated $C_{39}H_{30}N_3O_4Fe$ 660.1594; found 660.1586; UV-vis (λ_{max}/nm, THF, (log ε/L mol^{-1} cm^{-1})): 522 (4.54), 486 (4.35), 456 (3.87).

Synthesis of **2**, 2-ferrocenylmethyl-9-(2-morpholinoethyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone

In a 100 ml round-bottomed flask intermediate **4** (0.20 g, 0.40 mmol) and ferrocenylmethylamine (0.40 g, 1.8 mmol) were dissolved in 25 ml of quinoline, stirred for 24 hrs, and then zinc acetate (0.10 g, 0.60 mmol) was added and the mixture heated at 160 °C for 10 hours. The cooled reaction was poured into 100 ml of 1 M HCl resulting in a precipitate, which was collected and washed with 400 ml of warm water and 200 ml of MeOH. The crude product was purified by column chromatography on silica gel eluted with 100:1 (v/v) CH_2Cl_2/MeOH in 31% yield (100 mg). $R_f = 0.10$ (DMSO); m.p. > 300 °C; ^{1}H NMR (DMSO-d_6, ppm, 30 °C): σ_H 8.67-8.60 (m, 8H, Ar-*H*), 5.16 (s, 2H, Fc-CH_2-N), 4.53 (s, 2H, Morph-CH_2-N), 4.26-4.24 (m, 9H, Fc-*H*), 1.97–2.95 (m, 10H, CH_2N(CH_2CH_2)$_2$O); IR (KBr, cm^{-1}): 3000-2800, 1765, 1720, 1633, 1558, 1594, 1036, 809, 863; HRMS (ES-ToF, m/z); calculated $C_{41}H_{32}N_3O_5Fe$ 702.1703; found 702.1691; UV-vis (λ_{max}/nm, THF, (log ε/L mol^{-1} cm^{-1})): 519 (4.11), 484 (3.90), 454 (3.50).

References

S1 (a) Y. Nagao, Y. Tanabe and T. Misono, *Nippon Kagaku Kaishi*, 1979, 4, 528; (b) Y. Nagao, N. Ishikawa, Y. Tanabe and T. Misono, *Chem. Lett.*, 1979, 5, 151; (c) M. P. Schmidt and W. Neugebauer, United States Patent Office No 1506545, 1924; (d) Y. Nagao, Y. Abe and T. Misono, *Dyes Pigm.*, 1985, 6, 303; (e) Y. Nagao and T. Misono, *Dyes Pigm.*, 1984, 5, 171.

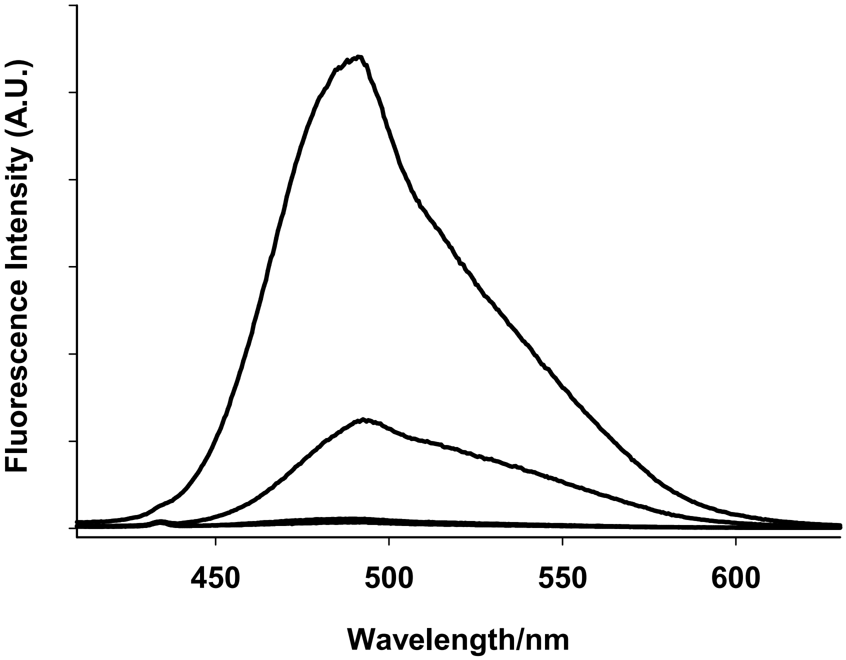
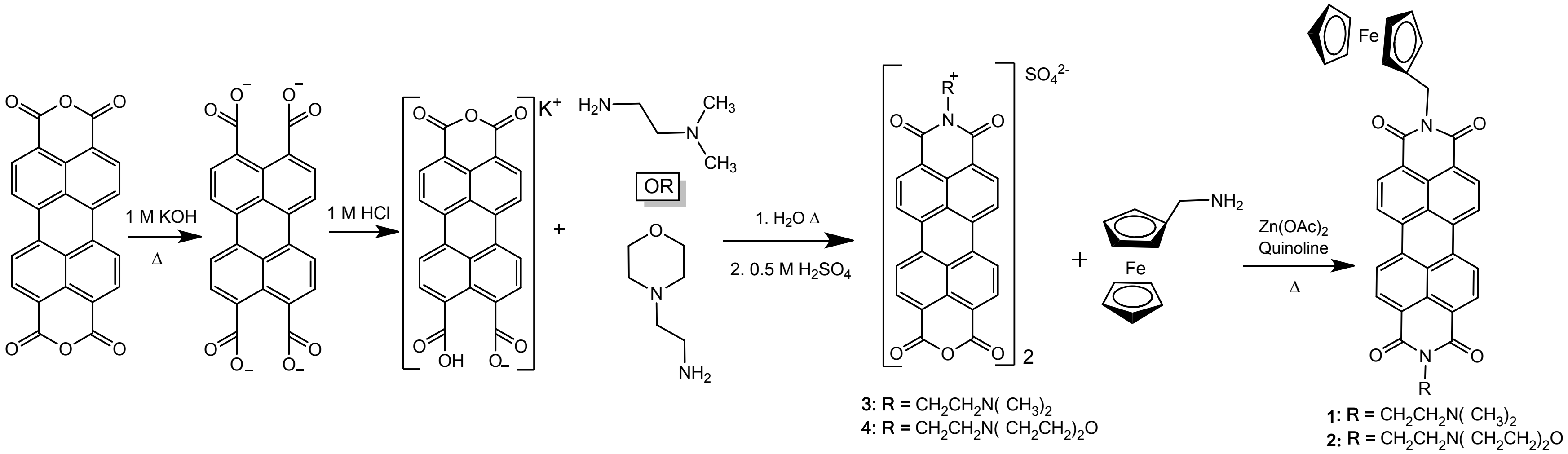
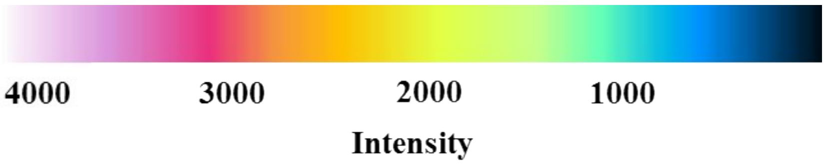


Fig. S1 Emission spectra of 10^{-6} M **3** in THF excited at 385 nm. High input conditions are 10 μM CH_3SO_3H and 10 μM $Fe(ClO_4)_3 \cdot H_2O$.



Scheme S1. . The synthesis of Pourbaix sensors **1** and **2**.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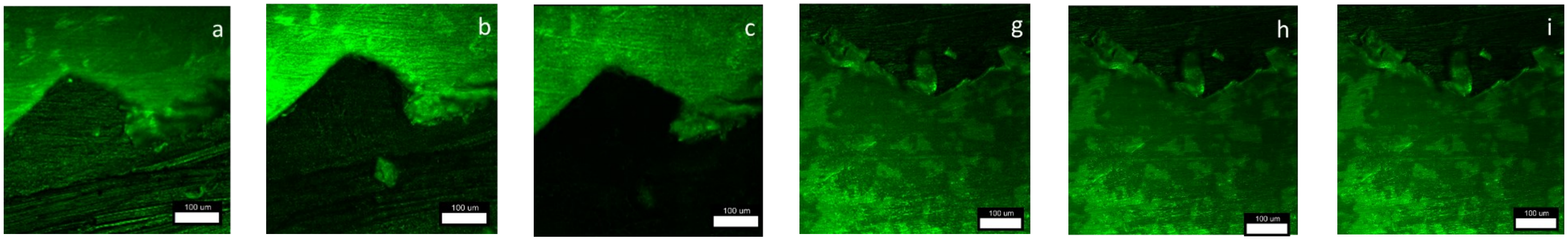
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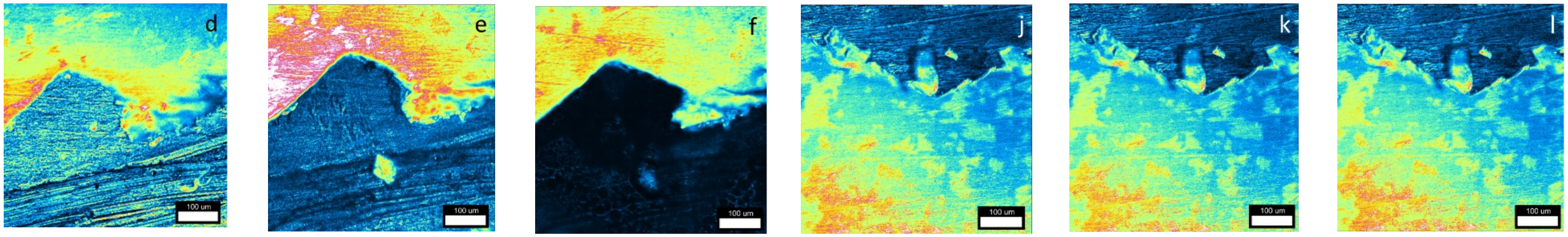

Fig. S2. Confocal microscope images of polyurethane coating impregnated with **2**. Confocal microscope images of a sample placed in a beaker of 0.5 M NaCl solution at **(a)** 0 min**; (b)** 90 min; **(c)** 24 hrs after exposure and a sample with DI water at **(g)** 0 min**; (h)** 90 min; **(i)** 24 hrs after exposure; enhanced contrast confocal microscope images of coupons exposed to 0.5 M NaCl solution at **(d)** 0 min; **(e)** after 90 min; **(f) after** 24 hrs exposure**;** and with DI water at **(j)** 0 min; **(k)** after 90 min; **(l)** 24 hrs after exposure. Molecule **2** at 13 µM/g. False colour legend inset on top left for **d-f** and **j-l.**

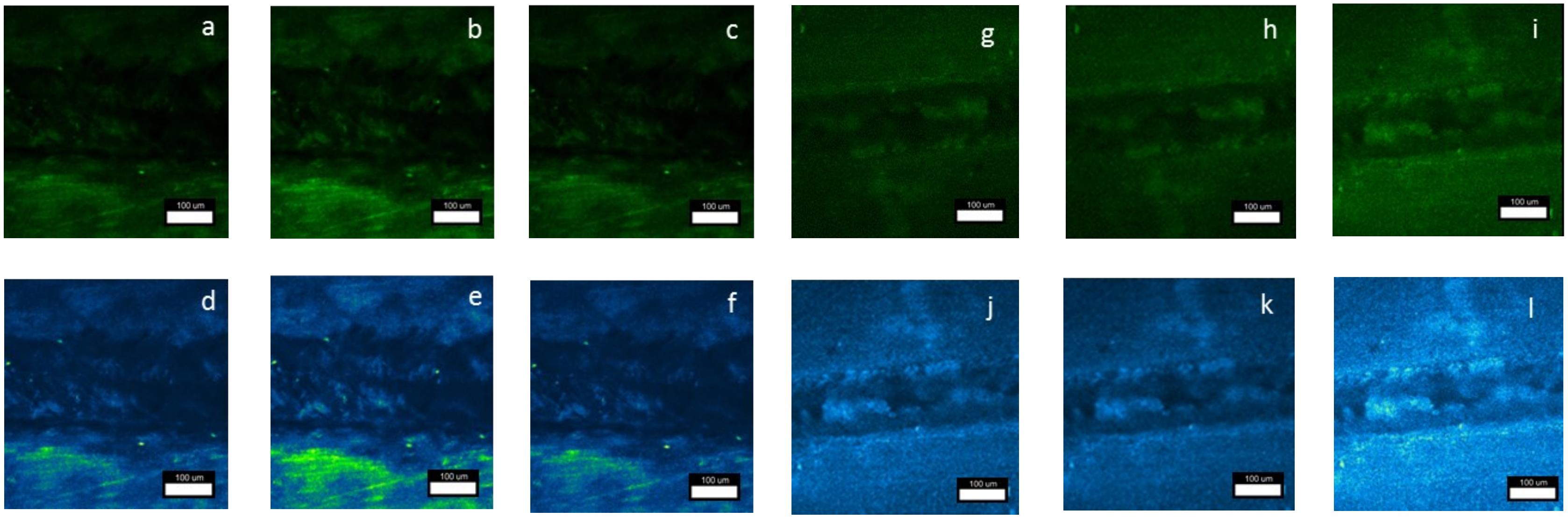

Fig. S3. Confocal microscope images of polyurethane coating impregnated with **3.** Confocal microscope images of a sample placed in a beaker of 0.5 M NaCl solution at **(a)** 0 min**; (b)** 90 min; **(c)** 24 hrs after exposure and a sample with DI water at **(g)** 0 min; **(h)** after 90 min; **(i)** after 24 hrs exposure; enhanced contrast confocal microscope images of coupons exposed to 0.5 M NaCl solution at (**d)** 0 min **(e)** after 90 min.; **(f)** after 24 hrs exposure**;** and with DI water at **(j)** 0 min; **(k)** after 90 min; **(l)** after 24 hrs exposure. Molecule **3** at 1.33 µM/g. False colour legend inset on top left for **d-f** and **j-l.**

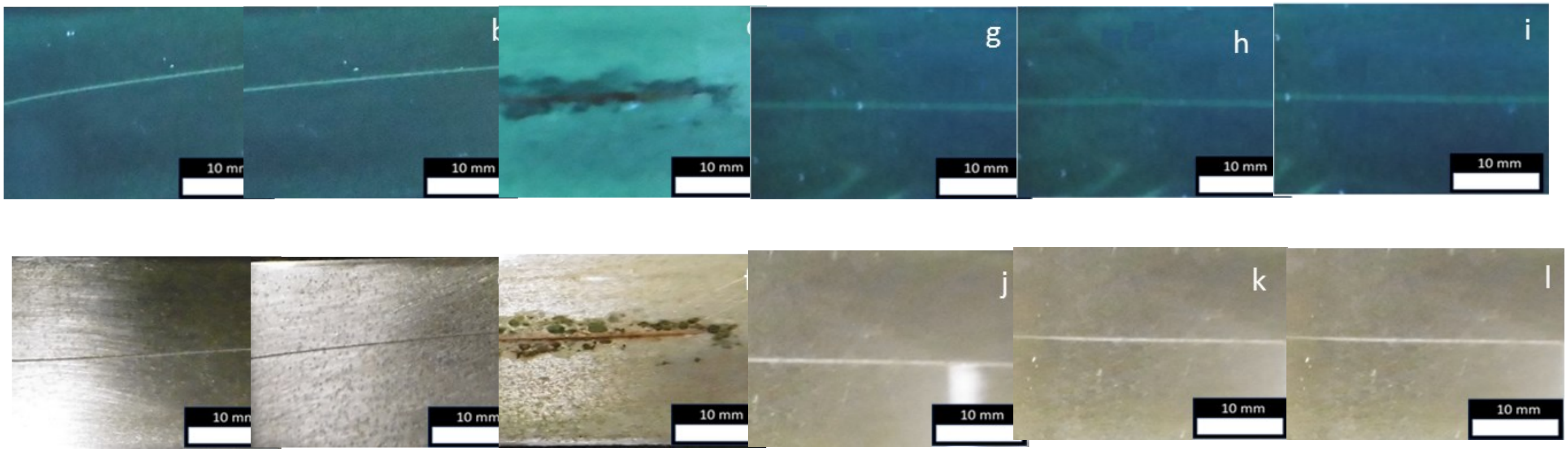

Fig. S4. Digital camera images of scratched metal coupons of **2** in a polyurethane coating under fluorescent 365 nm UV light under **a-c** and **g-i** and under ambient light **d-f** and **j-l.** Scratched area after exposure to 0.5 M NaCl solution at (**a**) 0 min; (**b**) after 90 min; (**c**) after 24 hrs under 365 nm UV light; images under ambient light at (**d**) 0 min, (**e**) 90 min and (**f**) 24 hrs after exposure, respectively; digital camera images of the scratched area after exposure to DI water at (**g**) 0 min; (**h**) after 90 min; (**i**) after 24 hrs under 365 nm UV light. Images under ambient light at (**j**) 0 min, (**k**) after 90 min and (**l**) after 24 hrs exposure respectively. Concentration of molecule **2** at 13.0 μM/g.

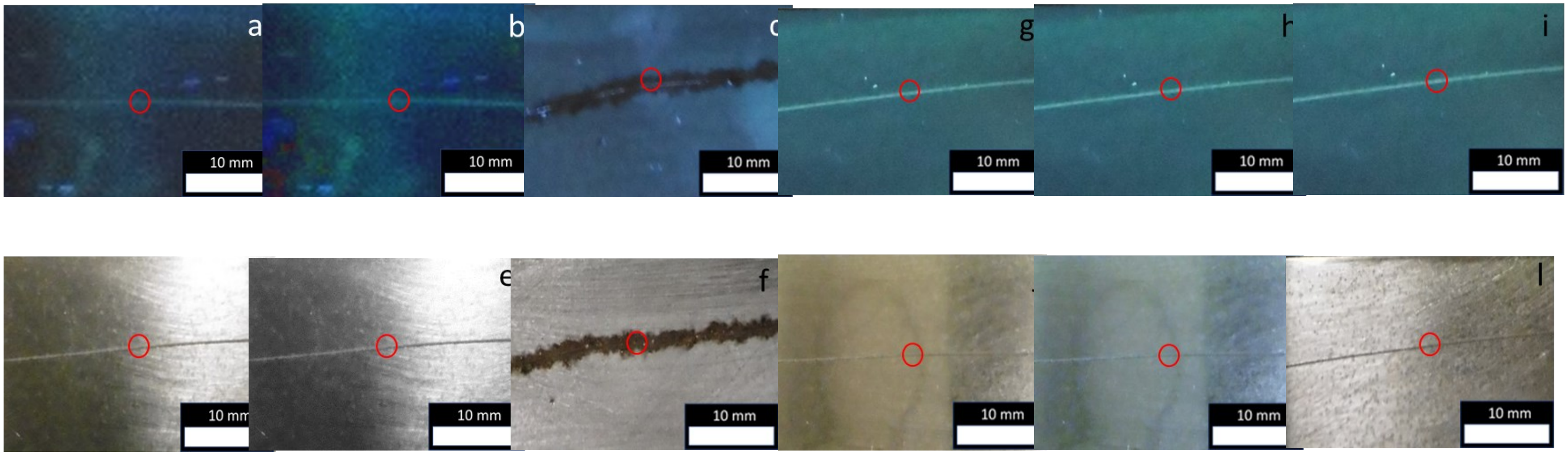

Fig. S5. Digital camera images of scratched metal coupons of **3** in a polyurethane coating under fluorescent 365 nm UV light **a-c, g-i** and under ambient light **d-f, j-l.** Scratched area after exposure to 0.5 M NaCl solution at (**a**) 0 min; (**b**) after 90 min; (**c**) after 24 hrs under 365 nm UV light; images under ambient light at (**d**) 0 min, (**e**) after 90 min and (**f**) after 24 hrs exposure, respectively; digital camera images of the scratched area after exposure to DI water at (**g**) 0 min; (**h**) after 90 min; (**i**) after 24 hrs exposure under 365 nm UV light. Images under ambient light at (**j**) 0 min, (**k**) after 90 min and (**l**) after 24 hrs exposure respectively. Concentration of molecule **3** at 1.33 μM/g.