Synthesis of Novel Photosensitive Polymers for the Protection of Mild Steel from Acid Corrosion

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(E)-1-(biphenyl-4-yl)-3-(4-(5-bromopentyloxy)phenyl)prop-2-en-1-one

In 100ml round-bottomed flask 4-[(1E)-3-(biphenyl-4-yl)buta-1,3-dien-1-yl]phenol (1g, 3.3mmol), anhydrous potassium carbonate (0.92 g, 6.6mmol), freshly distilled acetonitrile (30 ml) and 1,5-dibromopentane (1.8 ml, 13.26mmol) were placed. Above mixture was refluxed at 70 °C for 12 hour and the solution was cooled at room temperature, washed with large amount of water and extracted using ethyl acetate. The organic layer was washed with brine solution dried over anhydrous sodium sulphate and solvent was removed under vacuum and purified by column chromatography. Compound obtained as yellow color solid Yield: 76%; mp 109-110 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 1.67 (m, J = 7.5 Hz, 2H), 1.90 (m, J = 8.0 Hz, 2H), 1.98 (m, J = 7.0 Hz, 2H), 3.47 (t, J = 6.5 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 7.43 (t, J = 6.5 (t, J = 6.= 7.5 Hz, 1H), 7.49 (d, J = 15.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.64 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 7.0 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 16.0 Hz, 1H), 8.12 (d, J = 8.5 Hz, 2H), ¹³C NMR (126 MHz, CDCl₃) δ ppm 24.81, 28.36, 32.45, 33.53, 67.77, 114.93, 119.66, 127.25, 127.30, 127.62, 128.16, 128.96, 129.04, 130.28, 137.24, 140.03, 144.64, 145.311, 161.13, 189.97. IR (KBr, cm-1) 732, 1029, 1170, 1216, 1422, 1474, 1601, 1647, 2857, 1942, 3055, 3440. *m/z*: 449.1446 (M⁺).





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(E)-3-(4-(5-azidopentyloxy)phenyl)-1-(biphenyl-4-yl)prop-2-en-1-one

(*E*)-1-(biphenyl-4-yl)-3-(4-(5-bromopentyloxy)phenyl)prop-2-en-1-one (0.8g,1.78mmol) in acetone (25ml) with sodium azide (0.347g, 5.34mmol). The above reaction mixture was refluxed at 65 °C for 12 hours and the solution was cooled at room temperature, washed with excess of water and extracted using ethyl acetate. The organic layer was washed with brine solution dried over anhydrous sodium sulphate and solvent was removed under vacuum and purified by column chromatography. Compound obtained as yellow color solid Yield: 68%; mp 101-102 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 1.60 (m, *J* = 8.0 Hz, 2H), 1.71 (m, *J* = 7.5 Hz, 2H), 1.87 (m, *J* = 7.5 Hz, 2H), 3.33 (t, *J* = 7.0 Hz, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.49 (d, *J* = 15.0 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 16.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 2H), ¹³C NMR (126 MHz, CDCl₃) δ ppm 23.38, 28.65, 28.73, 51.34, 67.78, 114.93, 119.69, 127.24, 127.29, 127.63, 128.16, 128.96, 129.04, 130.28, 137.25, 140.03, 144.65, 145.31, 161.15, 189.98. IR (KBr, cm⁻¹) 736, 767, 820, 833, 845, 914, 989, 1032, 1177, 1245, 1265, 1307, 1293, 1474, 1510, 1602, 1659, 2113, 2863, 2937, 3037, 3055, 3445. *m/z*: 411.4981 (M⁺).





(*E*)-(*1*-(*5*-(*4*-(*3*-(*biphenyl*-*4*-*yl*)-*3*-*oxoprop*-*1*-*enyl*) *phenoxy*) *pentyl*)-1*H*-1, 2, 3-*triazol*-4-*yl*) *methyl acrylate*

500 mg of (*E*)-3-(4-(5-azidopentyloxy) phenyl)-1-(biphenyl-4-yl) prop-2-en-1-one was dissolved in 10 ml of DMSO:water (90:10) mixture with 2mg of copper iodide was added. To the above solution was stirred at room temperature then 0.1 ml of propargyl acrylate was added, after 48 hours the solution was poured in a 100 ml water and precipitate was observed. The precipitate was then filtered, washed with hexane and dried. Compound obtained as white solid Yield: 65%; mp 106-117 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 1.56 (m, *J* = 7.5 Hz, 2H), 1.87 (m, *J* = 6.0 Hz, 2H), 2.03 (m, *J* = 7.0 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 4.41 (t, *J* = 7.5 Hz, 2H), 5.34(s, 2H), 5.87 (dd, *J* = 10.5 Hz, 1H), 6.16 (dd, *J* = 17.0 Hz, 1H), 6.46 (dd, *J* = 17.5 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 15.0 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 15.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), ¹³C NMR (126 MHz, CDCl₃) δ ppm 23.17, 28.51, 29.96, 50.24, 57.74, 67.52, 114.89, 119.73, 123.76, 127.25, 127.29, 127.70, 128.01, 128.16, 128.96,

129.04, 130.28, 131.51, 137.21, 140.02, 144.59, 145.33, 161.00, 166.04, 189.98. IR (KBr, cm⁻¹) 737, 768, 806, 835, 1050, 1173, 1219, 1212, 1257, 1292, 1408, 1472, 1510, 1572, 1603, 1572, 1655, 1722, 2855, 1925, 3063, 3436. *m/z*: 520.744 (M⁺).





(E)-1-(biphenyl-4-yl)-3-(4-(6-bromohexyloxy)phenyl)prop-2-en-1-one

In 100ml round-bottomed flask 4-[(1E)-3-(biphenyl-4-yl)buta-1,3-dien-1-yl]phenol (1g, 3.3mmol), anhydrous potassium carbonate (0.92 g, 6.6mmol), freshly distilled acetonitrile (30 ml) and 1,6-dibromohexane (2.04 ml, 13.26mmol) was placed. Above mixture was refluxed at 70 °C for 12 hours, after the solution was cooled at room temperature, washed with excess of water and extracted using ethyl acetate. The organic layer was washed with brine solution dried over anhydrous sodium sulphate and solvent was removed under vacuum and purified by column chromatography. Compound obtained as yellow color solid Yield: 74%; mp 107-108 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 1.55 (m, J = 3.5 Hz, 4H), 1.85 (m, J = 7.0 Hz, 2H), 1.93 (m, J =7.0 Hz, 2H), 3.46 (t, J = 7.0 Hz, 2H), 4.04 (t, J = 6.5 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 7.43 (t, J = 6.5 (t, J = 6.= 7.5 Hz, 1H), 7.49 (d, J = 15.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 7.0 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 15.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 2H)¹³C NMR (126 MHz, CDCl₃) δ ppm 25.28, 27.90, 29.00, 32.65, 33.76, 67.92, 114.93, 2H). 119.62, 127.24, 127.29, 127.55, 128.16, 128.96, 129.04, 130.28, 137.25, 140.03, 144.69, 145.30, 161.23, 189.99. IR (KBr, cm⁻¹) 576, 693, 742, 813, 829, 985, 1030, 1170, 1216, 1251, 1291, 1422, 1507, 1584, 1601, 1647, 2858, 2916, 1943, 3028, 3056, 3436. *m/z*: 462.7989 (M⁺).





(E)-3-(4-(6-azidohexyloxy)phenyl)-1-(biphenyl-4-yl)prop-2-en-1-one

(*E*)-1-(biphenyl-4-yl)-3-(4-(6-bromopentyloxy)phenyl)prop-2-en-1-one (0.8g,1.72mmol) in acetone (25ml) with sodium azide (0.335g, 5.16mmol). The above reaction mixture was refluxed at 65 °C for 12 hours and the solution was cooled at room temperature, washed with excess of water and extracted using ethyl acetate. The organic layer was washed with brine solution dried over anhydrous sodium sulphate and solvent was removed under vacuum and purified by column chromatography. Compound obtained as yellow color solid Yield: 67%: mp 96-97 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 1.47-1.56 (m, *J* = 8.0 Hz, 4H), 1.67 (m, *J* = 7.0 Hz, 2H), 1.85 (m, *J* = 8.0 Hz, 2H), 3.31 (t, *J* = 7.0 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.49 (d, *J* = 15.0 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 7.0 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 16.0 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 2H), ¹³C NMR (126 MHz, CDCl₃) δ ppm 25.66, 26.51, 28.80, 29.04, 51.38, 67.92, 114.93, 119.63, 127.24, 127.29, 127.56, 128.16, 128.96, 129.04, 130.28, 137.25, 140.03, 144.67, 145.30, 161.23, 189.96. IR (KBr, cm⁻¹) 695, 732, 744, 770, 815, 833, 916, 1006, 1031,

1178, 1216, 1246, 1265, 1297, 1343, 1427, 1471, 1513, 1600, 1648, 2854, 2942, 3030, 3427. *m/z*: 425.3810 (M⁺).





(E)-(1-(6-(4-(3-(biphenyl-4-yl)-3-oxoprop-1-enyl)phenoxy)hexyl)-1H-1,2,3-triazol-4-yl)methyl acrylate

500 mg of (E)-3-(4-(6-azidohexyloxy)phenyl)-1-(biphenyl-4-yl)prop-2-en-1-one was dissolved in 10 ml of DMSO:water (90:10) mixture with 2mg of copper iodide was added. To the above solution was stirred at room temperature then 0.1 ml of propargyl acrylate was added, after 48 hours the solution was poured in a 100 ml water and precipitate was observed. The precipitate was then filtered, washed with hexane and dried. Compound obtained as white solid Yield: 65%; mp 111-112 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 1.43 (m, *J* = 8.0 Hz, 2H), 1.55 (m, *J* = 7.5 Hz, 2H), 1.82 (m, *J* = 8.0 Hz, 2H), 1.97 (m, *J* = 7.5 Hz, 2H), 4.01 (t, *J* = 6.0 Hz, 2H), 4.38 (t, *J* = 7.0 Hz, 2H), 5.33(s, 2H), 5.87 (dd, *J* = 10.5 Hz, 1H), 6.16 (dd, *J* = 17.0 Hz, 1H), 6.46 (dd, *J* = 17.0 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.49 (d, *J* = 15.0 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 16.0 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 2H), ¹³C NMR (126 MHz, CDCl₃) δ ppm 25.50, 26.23, 28.90, 30.15, 50.29, 57.75, 67.78, 114.91, 119.66, 123.74, 127.24, 127.28, 127.59, 128.02, 128.16, 128.95, 129.04, 130.28, 131.49, 137.22, 140.01, 144.64, 145.31, 161.15, 166.03, 189.98. IR (KBr, cm⁻¹) 741, 772, 808, 820, 976, 1031, 1176, 1190, 1203, 1256, 1293, 1406, 1463, 1511, 1574, 1604, 1655, 1729, 2856, 2937, 3068, 3426. *m/z*; 535.5324 (M⁺).





(E)-1-(biphenyl-4-yl)-3-(4-(10-bromodecyloxy)phenyl)prop-2-en-1-one

In 100ml round-bottomed flask 4-[(1E)-3-(biphenyl-4-yl)buta-1,3-dien-1-yl]phenol (1g, 3.3mmol), anhydrous potassium carbonate (0.92 g, 6.6mmol), freshly distilled acetonitrile (30 ml) and 1,10-dibromodecane (2.97 ml, 13.26mmol) were placed. Above mixture was refluxed at 70 °C for 12 hours and the solution was cooled at room temperature, washed with large amount of water and extracted using ethyl acetate. The organic layer was washed with brine solution dried over anhydrous sodium sulphate and solvents are removed under vacuum and purified by column chromatography. Compound obtained as yellow color solid Yield: 73%; mp 86-87 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 1.32-1.38 (m, 8H), 1.44-1.51 (m, 4H), 1.83 (m, J = 6.5 Hz, 2H), 1.88 (m, J = 7.0 Hz, 2H), 3.43 (t, J = 7.0 Hz, 2H), 4.03 (t, J = 6.5 Hz, 2H), 6.96 (d, J = 9.0Hz, 2H), 7.43 (t, J = 7.5 Hz, 1H), 7.49 (d, J = 15.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 7.0 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 15.5 Hz, 1H), 8.12 (d, J = 8.5 Hz, 2H), ¹³C NMR (126 MHz, CDCl₃) δ ppm 25.99, 28.15, 28.73, 29.15, 29.30, 29.35, 29.42, 32.81, 34.02, 68.19, 114.95, 119.57, 127.24, 127.29, 127.46, 128.15, 128.95, 129.03, 130.26, 137.27, 140.05, 144.73, 145.29, 161.34, 190.00. IR (KBr, cm⁻¹) 596, 689, 736, 766, 819, 835, 989, 1014, 1114, 1177, 1245, 1267, 1308, 1401, 1420, 1510, 1601, 1627, 1657, 2849, 2918, 3037, 3431. *m/z*: 518.0760 (M⁺).





(E)-3-(4-(10-azidodecyloxy)phenyl)-1-(biphenyl-4-yl)prop-2-en-1-one

(*E*)-1-(biphenyl-4-yl)-3-(4-(10-bromodecyloxy)phenyl)prop-2-en-1-one (0.8g,1.54mmol) in acetone (25ml) with sodium azide (0.3g, 4.62mmol). To the above reaction mixture was refluxed at 65 °C for 12 hours and the solution was cooled at room temperature, washed with excess of water and extracted using ethyl acetate. The organic layer was washed with brine solution dried over anhydrous sodium sulphate and solvents are removed under vacuum and purified by column chromatography. Compound obtained as yellow color solid Yield: 68%; mp 80-81 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 1.33-1.40 (m, 10H), 1.46-1.53 (m, 2H), 1.62 (m, *J* = 7.0 Hz, 2H), 1.83 (m, *J* = 6.5 Hz, 2H), 3.28 (t, *J* = 7.0 Hz, 2H), 4.03 (t, *J* = 6.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 15.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.68 (d, *J* = 7.0 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 15.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), ¹³C NMR (126 MHz, CDCl₃) δ ppm 25.99, 26.70, 28.83, 29.11, 29.15, 29.30, 29.38, 29.41, 51.49, 68.19, 114.19, 119.60, 127.23, 127.29, 127.48, 128.14, 128.94, 129.02, 130.25, 137.28, 140.05, 144.73, 145.29, 161.35, 190.01. IR (KBr, cm⁻¹) 689, 736, 766, 820, 834, 989, 1016, 1177, 1246, 1267, 1294, 1307, 1420, 1474, 1510, 1602, 1652, 2096, 2850, 2919, 3037, 3055, 3428. *m*/z: 480.1578 (M⁺).





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(E) - (1 - (10 - (4 - (3 - (biphenyl - 4 - yl) - 3 - oxoprop - 1 - enyl)phenoxy) decyl) - 1H - 1, 2, 3 - triazol - 4 - yl) methylacrylate

500 mg of (E)-3-(4-(10-azidodecyloxy)phenyl)-1-(biphenyl-4-yl)prop-2-en-1-one was dissolved in 10 ml of DMSO:water (90:10) mixture with 2mg of copper iodide was added. To the above solution was stirred at room temperature then 0.1 ml of propargyl acrylate was added, after 48 hours the solution was poured in a 100 ml water and precipitate was observed. The precipitate was then filtered, washed with hexane and dried. Compound obtained as white solid Yield: 65%; mp 92-93 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 1.32-1.40 (m, 10H), 1.45-1.53 (m, 2H), 1.82 (m, J = 6.5 Hz, 2H), 1.92 (m, J = 8.5 Hz, 2H), 4.02 (t, J = 6.5 Hz, 2H), 4.36 (t, J = 6.5 H 7.5 Hz, 2H), 5.33 (s, 2H), 5.87 (dd, J = 10.5 Hz, 2H), 6.15 (dd, J = 17.0 Hz, 2H), 6.45 (dd, J = 10.5 Hz, 2H), 6.15 (dd, J = 10.5 Hz, 2H), 7.5 (dd, J = 10.5 Hz, 2H), 7.5 (dd 17.5 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 7.42 (t, J = 7.5 Hz, 1H), 7.49 (d, J = 15.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.63 (broad d, J = 7.5 Hz, 3H), 7.67 (d, J = 7.0 Hz, 2H), 7.75 (d, J = 8.5 Hz, 3H)2H), 7.84 (d, J = 15.5 Hz, 1H), 8.12 (d, J = 8.5 Hz, 2H), ¹³C NMR (126 MHz, CDCl₃) δ ppm 25.97, 26.45, 28.93, 29.14, 29.26, 29.36, 30.21, 50.43, 57.78, 68.17, 114.95, 119.62, 123.75, 127.23, 127.28, 127.49, 128.06, 128.14, 128.94, 129.02, 130.25, 131.40, 137.27, 140.05, 142.78, 144.70, 145.29, 161.33, 166.02, 189.99. IR (KBr, cm⁻¹) 697, 743, 771, 827, 913, 986, 1006, 1033, 1175, 1219, 1263, 1295, 1406, 1470, 1511, 1571, 1591, 1604, 1654, 1726, 2851, 2927, 3032, 3064, 3428. *m/z*: 590.1777 (M⁺).







Fig. S1. GPC chromatogram of polymers



Fig. S2. Absorption spectral change of BI-5 solution during UV irradiation.



Fig. S3. Absorption spectral change of BI-6 solution during UV irradiation



Fig. S4. Extend of photo reaction vs. irradiation time.



Photo-cross-linkable mechanism of polymers



Fig. S5. Tafel curves of polymers in presence of BI-5 before and after cross-linking and absence of BI-5



Fig. S6. Tafel curves of polymers in presence of BI-6 before and after cross-linking and absence



Fig. S7. Bode plots for mild steel in presence of BI-5 before and after cross-linking and absence

of BI-5



Fig. S8. Bode plots for mild steel in presence of BI-6 before and after cross-linking and absence

of BI-6



Fig. S9. Nyquist plot of polymer in presence of BI-5 before and after cross-linking and absence



Fig. S10. Nyquist plot of polymer in presence of BI-6 before and after cross-linking and absence of BI-6

of BI-5



Fig. S11. Fitting of the corrosion data of mild steel in the presence of BI-5, BI-5C to Langmuir adsorption isotherm at different concentrations.



Fig. S12. Fitting of the corrosion data of mild steel in the presence of BI-6, BI-6C to Langmuir adsorption isotherm at different concentrations.





Fig. S13. SEM images and EDX spectra of (c) BI-5, (d) BI-5C, (e) BI-6 and (f) BI-10C