# Supplementary Information

## Synthesis of 4-Substituted Catechols with Side-Chains of Different C=C Bond Number as Urushiol Analogues and Their Anticorrosion Performance

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**1. Synthesis of 4-((4-Bocpiperazin-1-yl)methyl)catechol (1)**.

The reductive amination reaction of 3,4-dihydroxybenzaldehyde with *N*-Boc-piperazine was carried out, followed by Boc deprotection to give the intermediate 4-((piperazin-1-yl)methyl)catechol. The intermediate was then subjected to react with stearic acid, oleic acid, linoleic acid, and α-linolenic acid, respectively, to give the final products. In detail, a round-bottom flask was charged $CH_3OH$ (50 mL), 3,4-dihydroxybenzaldehyde (5.52 g, 40 mmol), *N*-Boc-piperazine (7.4 g, 40 mmol) and two drops acetic acid. The mixture was stirred at 40°C room temperature for 4 h under $N_2$. $NaBH_3CN$ (7.56 g, 120 mmol) was then added at room temperature for 24 h with magnetic stirring. After evaporated methanol, the resultant solution pH was adjusted to about 2 using dilute hydrochloric acid and then washed with ethyl acetate (3×100 mL) to recover catechol. Subsequently, the aqueous phase was adjusted to pH 8 with dilute NaOH solution and then extracted with 5×100 mL of ethyl acetate. The combined organic phase was dried over anhydrous $Na_2SO_4$ and evaporated to afford a mixture. The mixture was dissolved in acetonitrile and then recrystallized to give the desired 4-((4-Boc-piperazin-1-yl)methyl)catechol in trace amount, represented as **1**.

**4-((4-Bocpiperazin-1-yl)methyl)catechol** (**1**). Yellow solid (91%). $^1$H NMR (600 MHz, $CDCl_3$, ppm): δ 6.87 (d, J = 7.9 Hz, 1H), 6.72 (s, 1H), 6.54 (d, J = 7.6 Hz, 1H), 3.74 (s, 2H), 2.56 (s, 6H), 1.46 (d, J = 1.0 Hz, 9H). $^{13}$C NMR (100 MHz, DMSO-*d*6): δ 156.1 (s), 145.0 (s), 142.9 (s), 124.7 (s), 121.6 (s), 121.5 (s), 80.7 (s), 59.4 (s), 50.6 (s), 44.0 (s), 27.9 (s). HRMS (ESI-TOF): calcd for [$C_{16}H_{24}N_2O_4$ + $H^+$] 309.1819, found 309.1828.

**2. Synthesis of 4-(piperazin-1-ylmethyl)catechol** (**2**).

A flask was charged with ethyl acetate (100 mL), **1** (6.16 g, 20 mmol) and concentrated hydrochloric acid (37 wt%, 25 mL), and magnetically stirred for 4 h at room temperature. Thereafter 50 mL water was added into the flask and the mixture was washed with ethyl acetate (3×100 mL). Next, the aqueous phase was adjusted to pH 8 with dilute NaOH solution and extracted by ethyl acetate (5×100 mL). The organic phases were combined, dried with anhydrous sodium sulfate, and concentrated by rotary evaporation to give a residue, which was recrystallized in acetonitrile to give the product **2** as a yellow solid in yield of 99%.

**4-(Piperazin-1-ylmethyl)catechol** (**2**). White solid (4.1 g, 99%). $^{1}$H NMR (600 MHz, DMSO- d6): δ 8.71 (s, 1H), 6.67 (s, 1H), 6.63 (d, J = 7.9 Hz, 1H), 6.48 (d, J = 7.9 Hz, 1H), 3.23 (d, J = 12.8 Hz, 2H), 2.65 (t, J = 4.6 Hz, 3H), 2.22 (s, 4H).

**3. Synthesis of urushiol analogs (CPA0~3).**

General procedure. To a round-bottom flask EDC·HCl (0.55 g, 2.9 mmol), a fatty acid (2.4 mmol) and $CH_3OH$ (50 mL) were added, after magnetic stirring at room temperature for 15 min, the flask was cooled in an ice bath and NHS (0.39 g, 2.9 mmol) and the intermediate **2** (0.5 g, 2.4 mmol) were added. The reaction was heated to 40°C overnight. After evaporated to dry, the mixture was dissolved in ethyl acetate (50 mL), washed with brine solution (3×30 mL), dried with anhydrous sodium sulfate, and concentrated in vacuo to give a residue. The residue was purified on silica gel using petroleum ether/AcOEt (1/1, v/v) as eluent to give an urushiol analogue.

**4-((4-Stearoylpiperazin-1-yl)methyl)catechol** (**CPA0**). $^{1}$H NMR (400 MHz, $CDCl_3$, ppm): δ 6.88 (d, J = 7.9 Hz, 1H), 6.73 (t, J = 7.8 Hz, 1H), 6.55 (d, J = 7.4 Hz, 1H), 3.77 (s, 2H), 3.57 (s, 2H), 2.62 (s, 4H), 2.37 – 2.27 (m, 2H), 1.67 – 1.55 (m, 2H), 1.27 (d, J = 19.1 Hz, 29H), 0.88 (t, J = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): δ 172.43 (s), 144.20 (d, *J* = 18.8 Hz), 128.14 (s), 121.61 (s), 116.51 (s), 115.01 (s), 62.41 (s), 52.88 (s), 52.27 (s), 45.39 (s), 41.39 (s), 33.34 (s), 31.93 (s), 29.90 – 29.23 (m), 25.41 (s), 22.70 (s), 14.15 (s). HRMS (ESI-TOF): calcd for [$C_{29}H_{50}N_2O_3$ + $H^+$] 475.3894, found 475.3889.

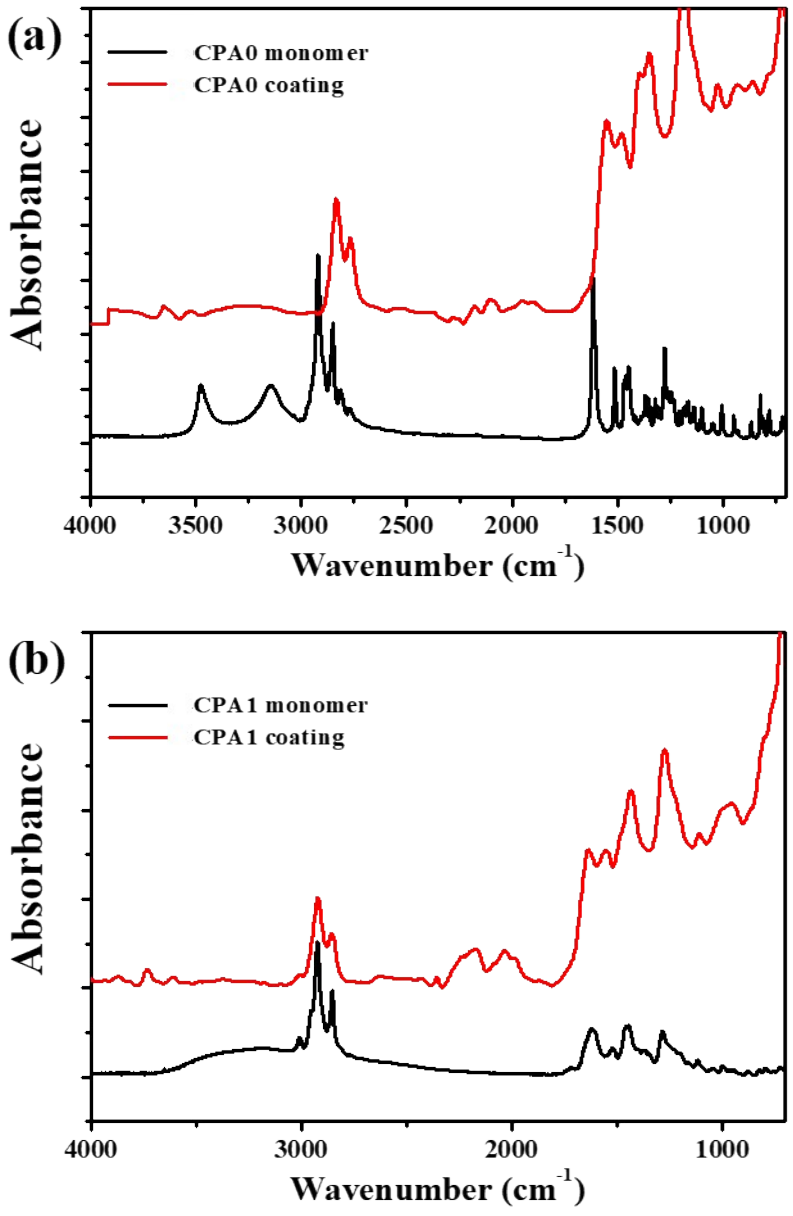
**4-((4-Oleoylpiperazin-1-yl)methyl)catechol** (**CPA1**). $^{1}$H NMR (400 MHz, $CDCl_3$, ppm): δ 6.82 – 6.71 (m, 2H), 6.63 (d, J = 8.0 Hz, 1H), 6.44 (s, 2H), 5.34 (dd, J = 12.3, 6.3 Hz, 3H), 3.61 (s, 2H), 3.45 (d, J = 20.4 Hz, 4H), 2.45 (d, J = 24.0 Hz, 4H), 2.31 (t, J = 7.6 Hz, 2H), 2.02 (dd, J = 16.1, 6.7 Hz, 4H), 1.60 (s, 2H), 1.28 (d, J = 13.2 Hz, 20H), 0.93 – 0.81 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): δ 172.44 (s), 144.28 (d, J = 16.6 Hz), 130.13 (d, J = 22.6 Hz), 129.71 (s), 127.89 (s), 121.68 (s), 116.62 (s), 115.09 (s), 62.33 (s), 52.79 (s), 52.19 (s), 45.32 (s), 41.35 (s), 33.31 (s), 31.91 (s), 31.52 (s), 29.81 – 28.96 (m), 27.20 (s), 25.64 (s), 25.38 (s), 22.63 (d, J = 11.4 Hz), 14.13 (s). HRMS (ESI-TOF): calcd for [$C_{29}H_{48}N_2O_3$ $^{+}$] 472.3738, found 472.3607.

**4-((4-Linoleoylpiperazin-1-yl)methyl)catechol** (**CPA2**). $^{1}$H NMR (400 MHz, $CDCl_3$, ppm): δ 6.75 (d, J = 12.4 Hz, 2H), 6.63 (d, J = 7.6 Hz, 1H), 5.48 – 5.22 (m, 3H), 3.61 (s, 2H), 3.43 (d, J = 25.1 Hz, 4H), 2.77 (s, 2H), 2.42 (d, J = 20.3 Hz, 6H), 2.34 – 2.26 (m, 3H), 2.04 (s, 4H), 1.60 (s, 2H), 1.28 (d, J = 13.7 Hz, 19H), 0.89 (s, 3H). $^{13}$C

NMR (100 MHz, $CDCl_3$, ppm): δ 172.33 (s), 144.43 (s), 144.08 (s), 130.24 (s), 130.03 (s), 129.73 (s), 128.52 (s), 127.97 (d, J = 16.0 Hz), 121.40 (s), 116.38 (s), 114.96 (s), 62.48 (s), 52.95 (s), 52.38 (s), 45.53 (s), 44.62 (s), 41.52 (s), 33.35 (s), 31.92 (s), 31.53 (s), 29.82 – 28.96 (m), 27.21 (s), 25.52 (d, J = 23.4 Hz), 22.65 (d, J = 11.2 Hz), 14.75 (s), 14.13 (s). HRMS (ESI-TOF): calcd for [$C_{29}H_{46}N_2O_3$ + $H^+$] 471.3581, found 471.3581.

**4-((4-Linolenylpiperazin-1-yl)methyl)catechol** (**CPA3**). $^1H$ NMR (400 MHz, $CDCl_3$, ppm): δ 6.81 – 6.72 (m, 2H), 6.65 (s, 1H), 5.41 – 5.28 (m, 6H), 3.61 (s, 2H), 3.44 (d, J = 25.4 Hz, 4H), 2.80 (d, J = 5.3 Hz, 4H), 2.42 (dd, J = 20.9, 6.0 Hz, 4H), 2.36 – 2.27 (m, 2H), 2.08 – 1.95 (m, 4H), 1.60 (s, 2H), 1.30 (s, 10H), 0.97 (t, J = 7.5 Hz, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) δ 172.25 (s), 144.32 (s), 144.01 (s), 131.97 (s), 130.25 (s), 128.52 (s), 128.26 (d, J = 5.4 Hz), 127.72 (s), 127.10 (s), 121.47 (s), 116.38 (s), 114.96 (s), 62.46 (s), 52.95 (s), 52.37 (s), 45.47 (s), 41.46 (s), 33.32 (s), 31.52 (s), 29.37 (dd, J = 27.9, 15.7 Hz), 27.20 (s), 25.79 – 25.23 (m), 22.58 (s), 20.55 (s), 14.30 (s), 14.10 (s). HRMS (ESI-TOF): calcd for [$C_{29}H_{46}N_2O_3$ + $H^+$] 469.3425, found 469.3425.

**4.** ***ATR-FTIR spectral comparison of CPA0, CAP1 and CPA3 with their coatings.***



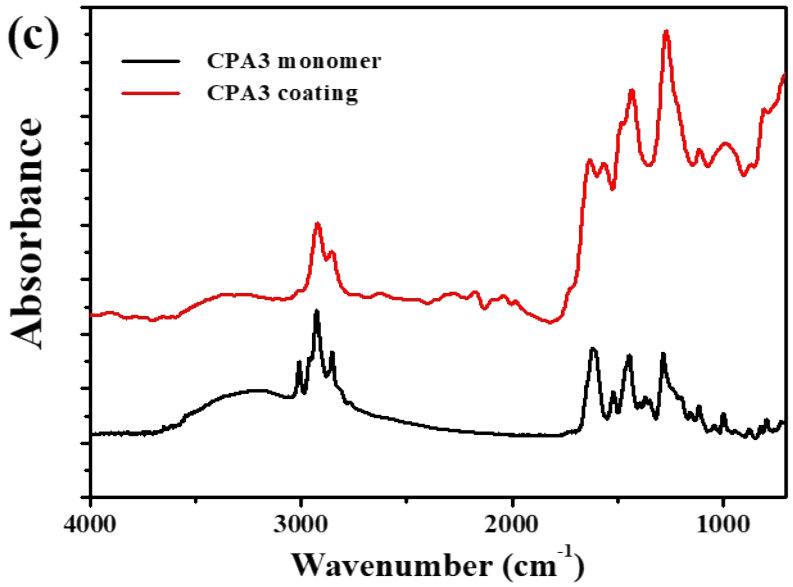



**Figure S1.** ATR-FTIR spectral comparison of CPA0, CAP1 and CPA3 monomer (a-c) with their coatings.