Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Spreading of Benquitrione Droplets on Superhydrophobic Leaves through Pillar[*5*]arene-based Host-guest Chemistry

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1. Computational methods

System setup: The 3-D structures of benquitrione and AP5A were built by Chem3D software. Then the geometry optimization of the structures was done by means of density functional theory with a hybrid function B3LYP. This was performed by Gaussian 09 suite of program at 6-31G (d) basis set.

Molecular docking technique was applied to obtain the binding conformation of benquitrione and AP5A. The molecular docking of benquitrione with AP5A was performed by DOCK version 6.6. AP5A was chose as the receptor with binding site covering the whole structure. And benquitrione was chose as the ligand allowed to be flexible during conformational search procedure. Docking results provide 20 candidate poses of benquitrione. The docked benquitrione + AP5A complexes were then submitted to energy minimization in all-atom AMBER force field and Generalized Born (GB) solvent using the AMBER16 program. The binding energy of these complexes were calculated by MM-PBSA method. The best complex conformation with the largest binding free energy was chose the final conformation for molecular dynamics simulation.

Thetrilayer graphene model was prepared by the nanotube builder plugin implemented in Visual Molecular Dynamics software. The graphene model contains 3 layers of graphene sheet with the area of 25 × 25 nm^2. A water droplet with diameters of 10 nm was prepared by Packmol software. The spherical space contains 17221 water molecules, which is consistent with the water density of 998.2 kg / m^3. Five molecule structures of benquitrione or benquitrione + AP5A complex are added into the water droplets to form the two solution systems, and the overlapping water molecules were deleted. Finally, the two solution spheres were then placed 0.2 nm away from the graphene surface to allow interactions and avoid irregular contact.

Molecular dynamics simulation: All the simulations were carried out by GROMACS 5.1 program with AMBER99 force field [28]. The TIP3P water model was chose for the topology information of water molecules. Carbon atoms in the graphene sheets are fixed throughout the simulations. The simulation cells are 25 × 25 × 30 nm^3 with periodic boundary conditions in all directions. Van der Waals interactions are cut off at 1.0 nm. The electrostatic force is computed using cut-off method with 1.0 nm electrostatic cut-off. V-rescale thermostat was used to control the temperature (300 K) of the simulated system with a time constant of 0.1 ps. Time step was set to 2 fs. 1 ns molecular dynamics simulations were performed at an NVT ensemble for each system.

2. The synthesis of AP5A

P5 (0.30 g, 0.30 mmol / L), cysteamine hydrochloride (1.50 g, 13.20 mmol / L), and 2, 2-dimethoxy-2-phenylacetophenone (0.10 mg, 0.40 mmol / L) were dissolved in a solution of Methanol and Dichloromethane (1 : 10). Once it was completely dissolved click reaction was carried out at 365 nm UV light under an oxygen and moisture free, N_2 (g) protected conditions. White color precipitate was filtered and washed thoroughly using the same solvent mixture used in this reaction to obtain the final product. Complex was confirmed by ^{1}H NMR spectrum using CD_3OD as the solvent.

Spectra analysis of AP5A: ^{1}H NMR (600 MHz, CD_3OD) δ (ppm): 6.82 (s, 10 H), 3.96-3.76 (s, 40 H), 3.17 (d, 20 H), 2.88 (s, 40 H), 2.13 (d, 20 H). These are in accord with the literature [27].

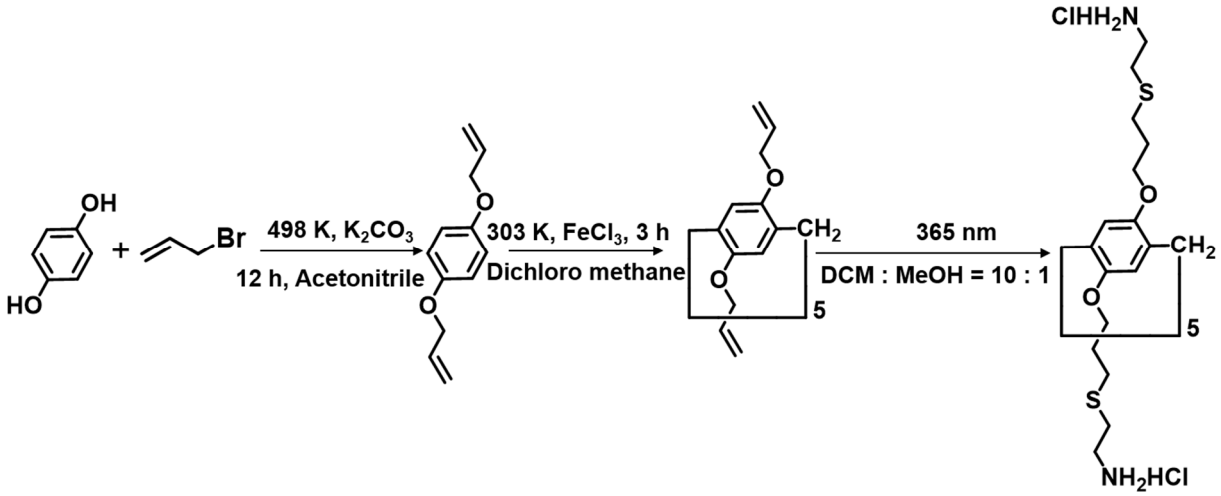

Figure S1. The synthetic route of the AP5A. P5 (0.30 g, 0.30 mmol / L), cysteamine hydrochloride (1.50 g, 13.20 mmol / L) 2, 2-dimethoxy–2-phenylacetophenone (0.10 mg, 0.40 mmol / L) were dissolved in a solution of Methanol and Dichloromethane (1 : 10). Once it was completely dissolved click reaction was carried out at 365 nm UV light under an oxygen and moisture free, N_2 (g) protected conditions. White color precipitate was filtered and washed thoroughly using the same solvent mixture used in this reaction to obtain the final product.

3. The synthesis of CP5A

P5 (0.30 g) is added to the anaerobic 2, 2-dimethoxy-2-phenyl acetophenone solvent (0.30 g), during which mercaptoacetic acid (ρ =1.33 g / ml, V = 0.82 ml) was injected, and O_2 was continuously evacuated. Dichloromethane also required an anaerobic state before being injected into the flask, and finally injected into the reactor.

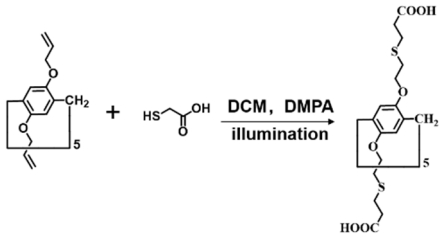

Figure S2. The synthetic route of the CP5A.

4. The synthesis of P5A

P5 (1.00 g) and NaN_3 are dissolved in DMF (25 ml) solvent and react overnight in oil bath 150^O without oxygen and N_2 protection. P5-N_3 (707 mg) was dissolved in a PPh_3 (oxygen-free, N_2 protected) solution, to which THF (20 ml) was added first, followed by H_2O (6 ml), and stirred overnight.

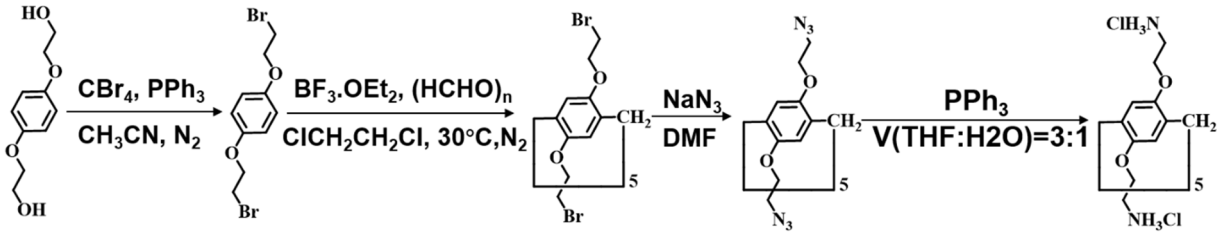

Figure S3. The synthetic route of the P5A.

5. ^{1}H NMR of AP5A

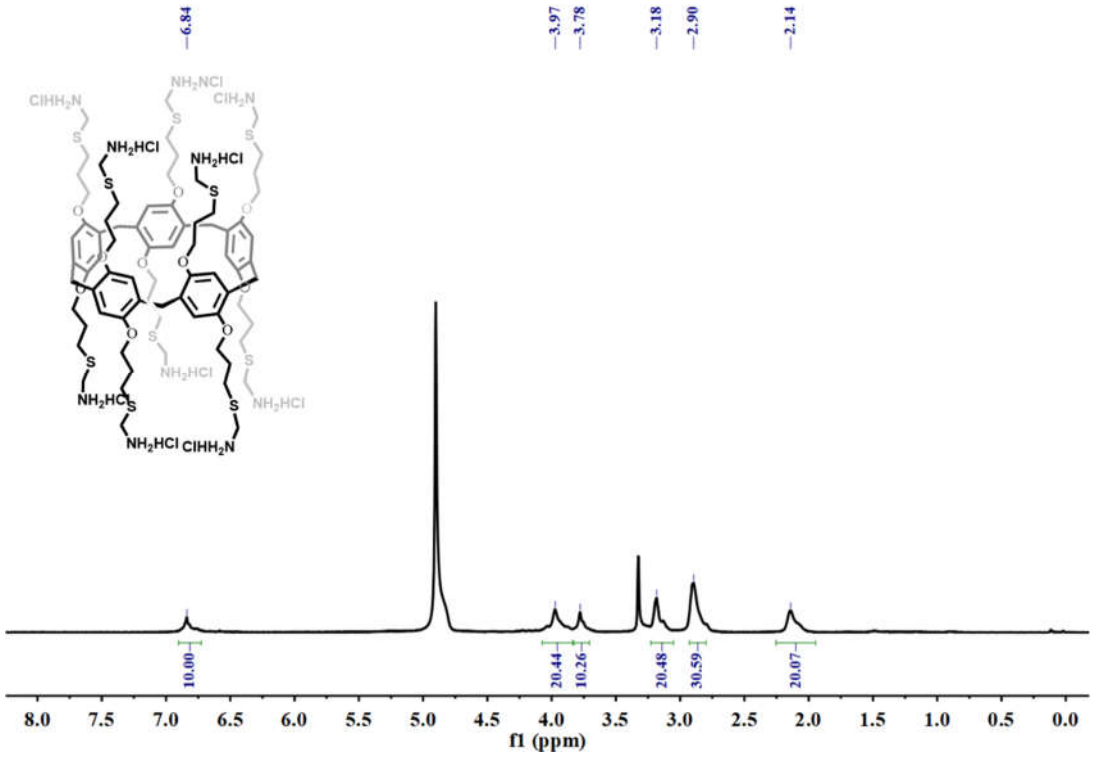

Figure S4. The ^{1}H NMR (CD_3OD, 600 MHz, 298 K) for AP5A.

6. ^{1}H NMR of CP5A

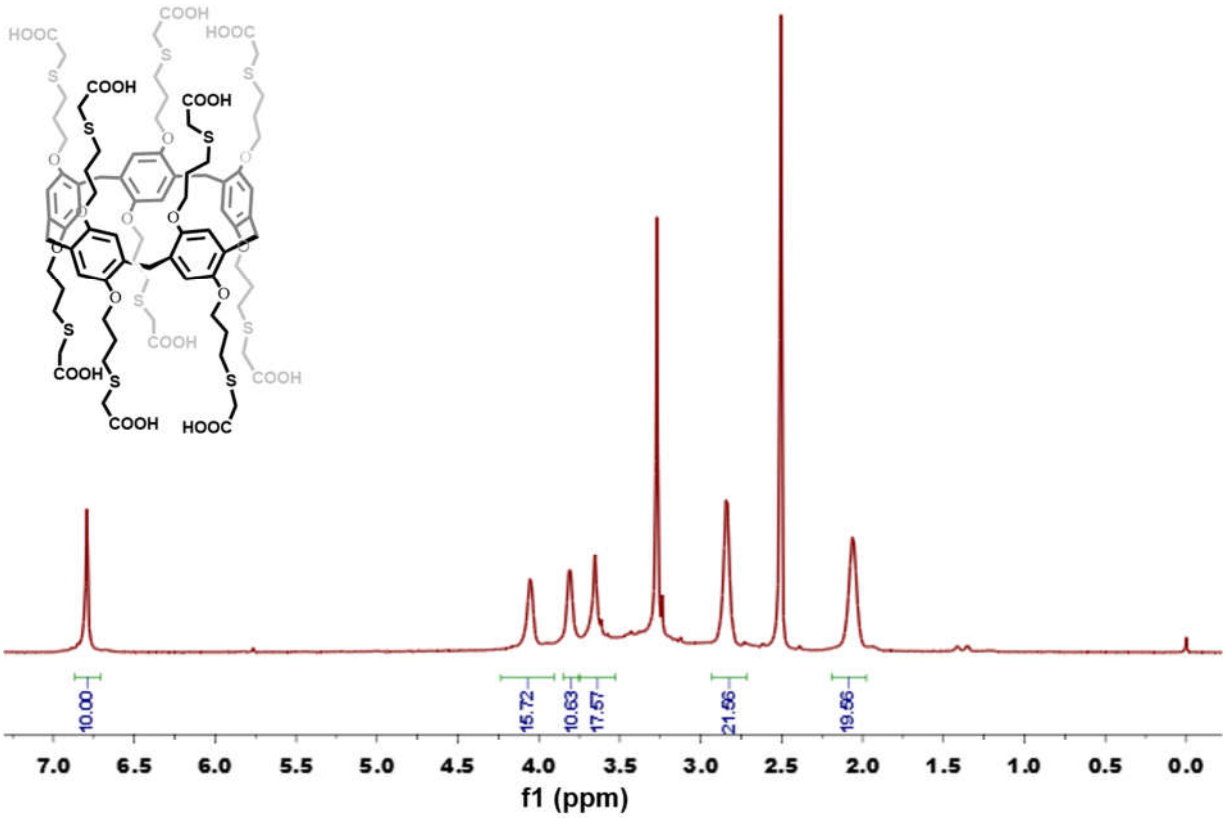

Figure S5. The ^{1}H NMR (DMSO, 600 MHz, 298 K) for CP5A.

7. ^{1}H NMR of P5A

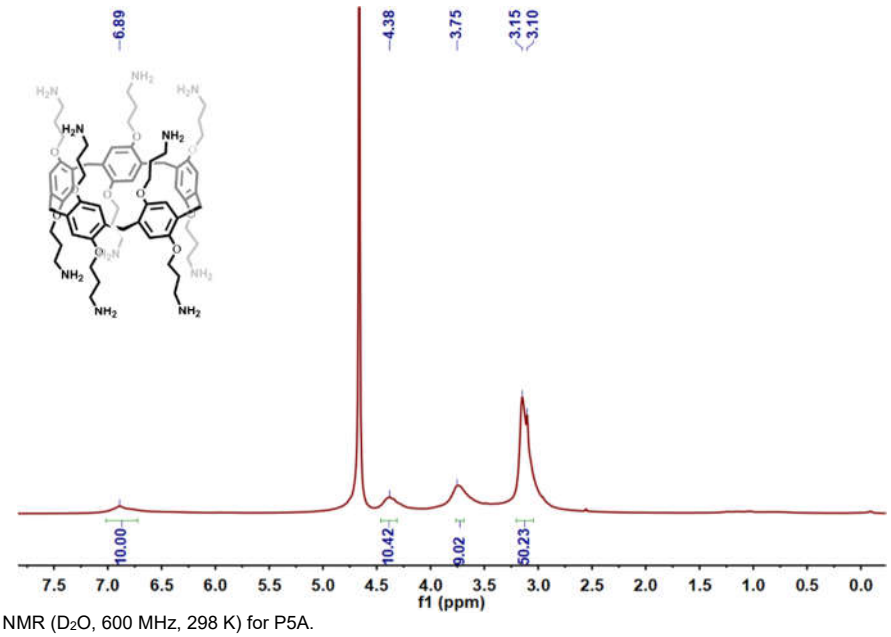

Figure S6. The ^{1}H NMR (D_2O, 600 MHz, 298 K) for P5A.

8. The UV spectra between benquitrione and CP5A, AP5A, P5A

Different concentrations of guest benquitrione aqueous solution (1.0 × 10^{-3} mol / L, 3 μL, 6 μL, 9 μL, 12 μL, 15 μL, 18 μL, 21 μL, 24 μL, 27 μL, 30 μL, 33 μL, 36 μL, 39 μL, 42 μL, 45 μL, 48 μL, 51 μL, 54 μL, 57 μL, 60 μL) were added to the host AP5A (1.0 × 10^{-5} mol / L, 3 mL) solution to quantify the binding ability of AP5A to benquitrione, and the absorption value of AP5A at 298 nm was gradually increased.

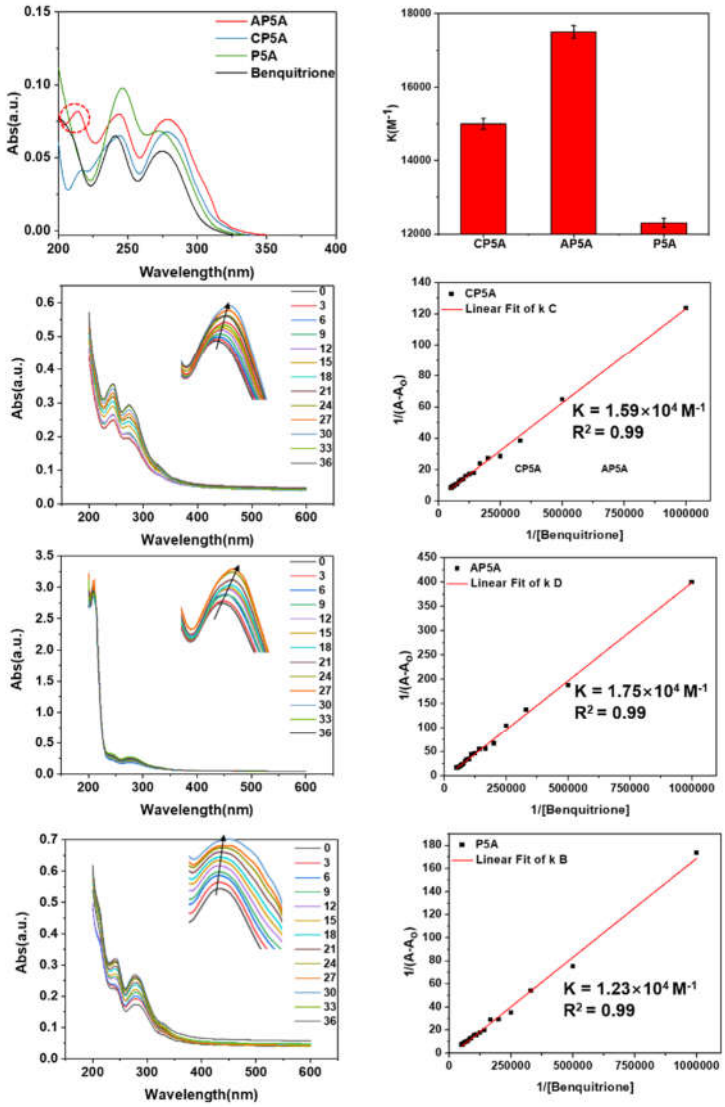

Figure S7. (a) The UV-Vis spectrum of benquitrione (3 mL, 10^{-5} mol/L) after adding CP5A, AP5A and P5A ((3 μL, 10^{-3} mol/L)). The dotted circle highlights the absorption peak of the ultraviolet spectrum at 217 nm was amplified; (b) Complexing constant of benquitrione with different hosts. The difference value 1 / (A-Ao) = 1 / (Δε × Ka [benquitrione]) × 1 / [Host] + 1 / (Δε × Ka [benquitrione]) was shown in the column diagram after the different hosts was added into benquitrione solution showing benquitrione is selective to AP5A. (c) UV titration experiments and a linear fitting curve based on the relationship between the change in absorption peak at 298 nm and the concentration of the guest. The Penesi-Hildebrand equation [24] is used to investigate the reciprocal of the increase in the value of the absorption intensity at 298 nm after the addition of benquitrione. The relationship between the reciprocal of benquitrione concentration (1 / [benquitrione]), data processing found that 1 / ($A-A_O$) and 1 / [benquitrione] relationship, the ratio of intercept to slope obtained by linear fitting shows that the binding constant of benquitrione to AP5A is K = 1.75×10^4 M^{-1}, which indicates that AP5A has good binding ability to guest.

9. The UV spectra between benquitrione and AP5A

By measuring the ratio of the amounts of different substances (n_{host} : n_{guest} = 9 : 1; 8 : 2; 7 : 3; 6 : 4; 5 : 5; 4 : 6; 3 : 7; 2 : 8 and 1 : 9). The UV spectra of the host-guest solution is used to investigate the absorption intensity of the AP5A benzene ring at 298 nm. Under the same conditions, only a series of UV-Vis spectral curves of the guest were added to investigate the absorption intensity value (A_O) of benzene ringof AP5A at 298 nm. Taking the ratio of ($A-A_O$) to the host-guest ratio, the Job curve is obtained.

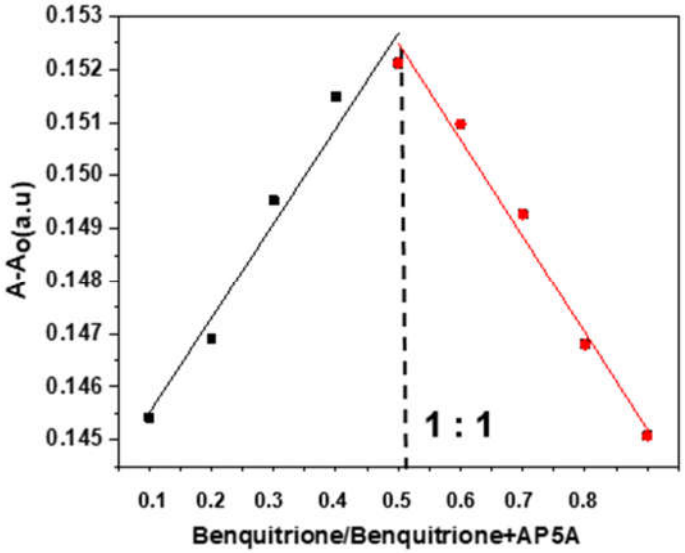

Figure S8. Experiment of the Job curve. The Job curve found that when the molar fraction of AP5A and benquitrione reached 0.5, the UV-Vis spectra had the largest difference at the 298 nm peak, indicating that the host-guest formed a 1 : 1 complex.

10. The gauss calculation of the interaction between benquitrione and different hosts

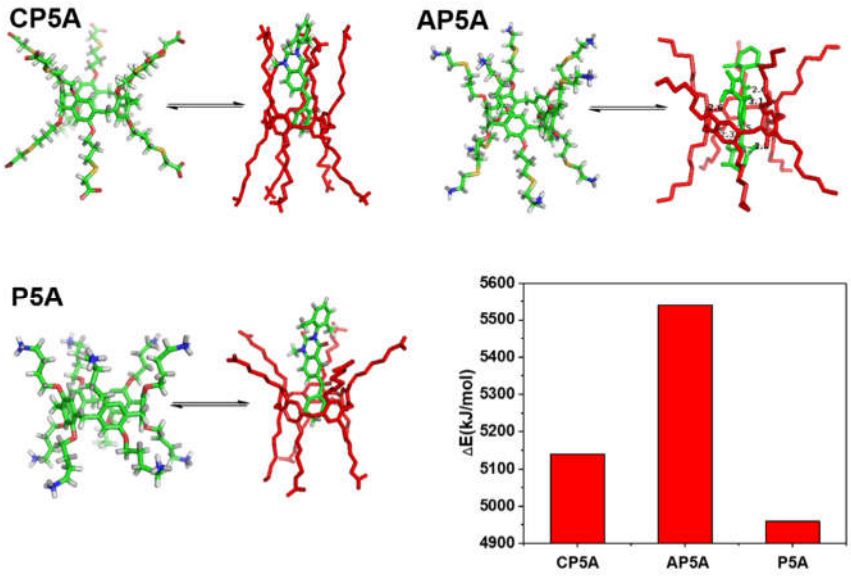

Figure S9. Optimization of CP5A, AP5A, P5A structure and combination model of benquitrione. The binding energy [$\Delta E_{binding\ energy} = E_{host+guest} - (E_{host} + E_{guest})$] is -5.14×10^3 kJ / mol, -5.54×10^3 kJ / mol, -4.96×10^3 kJ / mol, respectively. It can be seen that the binding of benquitrione and AP5A is the most stable. Benquitrione can be selectively entrapped in the cavity of AP5A with a binding ratio of 1 : 1.

Table S1. Energy change of benquitrione and AP5A by the Gaussian simulation.

Item	Energy(kJ / mol)
Host (AP5A)	-2.25×10^7
Guest (benquitrione)	-3.69×10^6
△E	-5.54×10^3

$\triangle E = E_{(benquitrione + AP5A)} - E_{(benquitrione)} - E_{(AP5A)}$

Three-dimensional coordinates of benquitrione and AP5A.

C(1)	-1.0242	1.941	-3.79
C(2)	-1.1643	0.6046	-4.1282
C(3)	-0.0636	-0.2163	-4.3562
C(4)	1.1945	0.3766	-4.2763
C(5)	1.334	1.6729	-3.8037
C(6)	0.2345	2.4782	-3.5263
C(7)	-0.2482	-1.6844	-4.7322
C(8)	-0.4041	-2.6214	-3.5375
C(9)	0.7091	-3.2011	-2.9356
C(10)	0.5935	-4.0551	-1.8504
C(11)	-0.6376	-4.2423	-1.2241
C(12)	-1.7551	-3.7106	-1.8599
C(13)	-1.6523	-2.9803	-3.034
C(14)	-0.7775	-5.0411	0.0691
C(15)	-0.6525	-4.2018	1.3382
C(16)	-1.7608	-3.6299	1.9611
C(17)	-1.5986	-2.7543	3.0227
C(18)	-0.3548	-2.5264	3.6049
C(19)	0.7193	-3.2602	3.1071
C(20)	0.5809	-4.0191	1.9548
C(21)	-0.2051	-1.5575	4.7746
C(22)	-0.0073	-0.1022	4.3589
C(23)	-1.0598	0.808	4.3211
C(24)	-0.872	2.083	3.8089
C(25)	0.3841	2.5537	3.4427
C(26)	1.4653	1.7016	3.6672
C(27)	1.2595	0.3855	4.0479
C(28)	0.5621	3.9599	2.8729
C(29)	0.5176	4.0367	1.3494
C(30)	-0.6879	4.037	0.6484
C(31)	-0.6982	3.9521	-0.7346
C(32)	0.4726	4.0106	-1.4853
C(33)	1.6641	4.1914	-0.7896
C(34)	1.6819	4.1412	0.598
C(35)	0.4229	3.9013	-3.0075

O(36)	-2.1412	2.7467	-3.7695
O(37)	-2.799	-2.6699	-3.7308
O(38)	-3.0339	-3.9793	1.5704
O(39)	-2.292	0.4747	4.8379
O(40)	-1.8648	4.0743	1.3475
O(41)	2.3108	-0.2954	-4.7189
O(42)	1.6971	-4.768	-1.4392
O(43)	1.916	-3.2921	3.7878
O(44)	2.7542	2.1759	3.574
O(45)	2.8363	4.4517	-1.4624
H(46)	-2.157	0.2073	-4.2426
H(47)	2.3275	2.0659	-3.6801
H(48)	-1.1192	-1.7661	-5.3676
H(49)	0.6014	-2.0128	-5.3141
H(50)	1.6894	-3.0138	-3.3362
H(51)	-2.7346	-3.8898	-1.4547
H(52)	-0.0224	-5.8146	0.0973
H(53)	-1.738	-5.5375	0.0599
H(54)	-2.4703	-2.2668	3.4214
H(55)	1.4548	-4.4984	1.5518
H(56)	0.6387	-1.8568	5.3806
H(57)	-1.0865	-1.6338	5.3957
H(58)	-1.7291	2.7227	3.7135
H(59)	2.114	-0.2622	4.1308
H(60)	1.5099	4.3632	3.202
H(61)	-0.2111	4.5956	3.2834
H(62)	-1.64	3.842	-1.2412
H(63)	2.6335	4.1992	1.0948
H(64)	1.3408	4.2944	-3.4205
H(65)	-0.3827	4.5254	-3.3711
H(66)	2.5081	3.4284	5.176
C(67)	3.2186	2.6962	4.8076
C(68)	4.5793	3.3664	4.6506
C(69)	5.7405	2.3844	4.4971
C(70)	7.3863	3.1615	4.3329
C(71)	7.7862	3.6631	6.0418

C(72)	9.2681	4.0332	6.0684
N(73)	9.6901	4.5262	7.4381
H(74)	8.9663	-1.7771	-10.8952
H(75)	7.3573	-1.7761	-11.1305
H(76)	7.8478	-7.5201	9.4174
H(77)	6.2759	-7.1866	9.6661
H(78)	10.6747	4.767	7.4525
H(79)	9.1824	5.3546	7.721
H(80)	9.7305	9.791	-4.3828
H(81)	8.1354	10.0299	-4.5883
H(82)	7.6848	-11.6547	-2.6211
H(83)	6.0617	-11.7238	-2.5498
H(84)	3.2666	1.897	5.542
H(85)	4.5518	4.0401	3.8017
H(86)	4.734	3.9773	5.5357
H(87)	5.7723	1.6801	5.3204
H(88)	5.6317	1.8089	3.5868
H(89)	7.1815	4.5091	6.3472
H(90)	7.5951	2.8379	6.7188
H(91)	9.897	3.1852	5.8442
H(92)	9.4966	4.8338	5.3806
H(93)	9.55	3.8278	8.1567
H(94)	2.1603	6.2564	-2.1564
C(95)	3.0444	5.8341	-1.6906
C(96)	4.2415	6.0629	-2.6077
C(97)	5.5929	5.8282	-1.9328
S(98)	7.0457	6.0454	-3.0194
C(99)	7.2249	7.858	-3.1406
C(100)	8.5912	8.1317	-3.7676
N(101)	8.8212	9.6158	-3.9701
H(102)	3.1827	6.3414	-0.7395
H(103)	4.1495	5.4238	-3.4785
H(104)	4.1825	7.0895	-2.9591
H(105)	5.7137	6.4608	-1.0609
H(106)	5.673	4.8019	-1.5981
H(107)	6.4378	8.2837	-3.752

H(108)	7.1728	8.2979	-2.1509
H(109)	9.3968	7.7831	-3.1396
H(110)	8.6843	7.6802	-4.7442
H(111)	8.7921	10.1308	-3.0996
H(112)	1.6461	-0.2947	-6.6564
C(113)	2.552	-0.0802	-6.1
C(114)	3.6703	-0.9799	-6.6153
C(115)	5.0714	-0.5319	-6.1994
S(116)	6.4293	-1.5883	-6.8151
C(117)	6.5865	-1.0962	-8.5659
C(118)	7.8965	-1.6872	-9.0846
N(119)	8.0942	-1.3865	-10.5567
H(120)	2.7917	0.9665	-6.2651
H(121)	3.4939	-1.9965	-6.2826
H(122)	3.5973	-0.984	-7.6994
H(123)	5.2643	0.4906	-6.5029
H(124)	5.1782	-0.5722	-5.1229
H(125)	5.7503	-1.4667	-9.1473
H(126)	6.6093	-0.0148	-8.6405
H(127)	8.7525	-1.2742	-8.5729
H(128)	7.917	-2.7632	-8.9954
H(129)	8.1277	-0.3926	-10.7439
H(130)	0.8493	-6.5418	-2.0123
C(131)	1.794	-6.0175	-2.1037
C(132)	2.8964	-6.8861	-1.5065
C(133)	4.3093	-6.4712	-1.9167
S(134)	5.643	-7.5237	-1.2438
C(135)	5.565	-9.0189	-2.2883
C(136)	6.835	-9.8248	-2.0204
N(137)	6.8387	-11.1252	-2.7987
H(138)	1.9675	-5.8494	-3.1629
H(139)	2.8095	-6.8842	-0.4259
H(140)	2.7077	-7.9037	-1.8372
H(141)	4.4109	-6.4334	-2.9951
H(142)	4.5403	-5.4836	-1.5383
H(143)	4.6878	-9.6095	-2.0511

H(144)	5.5182	-8.732	-3.3329
H(145)	7.7213	-9.2879	-2.3223
H(146)	6.9261	-10.1004	-0.9803
H(147)	6.7938	-10.974	-3.7982
H(148)	1.0521	-4.2235	5.3937
C(149)	1.936	-4.3133	4.7722
C(150)	3.1717	-4.2115	5.6608
C(151)	4.455	-4.7246	5.0075
S(152)	5.9413	-4.6434	6.0677
C(153)	5.7224	-6.0518	7.2084
C(154)	7.0543	-6.2639	7.9262
N(155)	6.9607	-7.3803	8.9467
H(156)	1.8896	-5.2834	4.2853
H(157)	3.303	-3.1826	5.976
H(158)	2.9644	-4.7926	6.5551
H(159)	4.3375	-5.7432	4.6561
H(160)	4.7137	-4.1174	4.1494
H(161)	4.9366	-5.8476	7.9263
H(162)	5.456	-6.9393	6.6452
H(163)	7.8388	-6.5451	7.2403
H(164)	7.3619	-5.3854	8.4737
H(165)	6.7119	-8.2658	8.525
H(166)	-2.7729	-5.9132	2.1919
C(167)	-3.5067	-5.1186	2.2706
C(168)	-4.8311	-5.6156	1.7007
C(169)	-6.0385	-4.7661	2.0973
S(170)	-7.641	-5.3632	1.4533
C(171)	-8.0304	-6.7766	2.541
C(172)	-9.492	-7.1474	2.2948
N(173)	-9.8998	-8.3579	3.1104
H(174)	-8.8567	1.1935	11.2491
H(175)	-3.9203	12.6396	4.3939
H(176)	-8.0733	6.2816	-8.5284
H(177)	-8.827	-5.2488	-8.8135
H(178)	-9.3534	-9.1779	2.88
H(179)	-9.7144	-5.1346	-9.2904

H(180)	-8.1143	-5.2953	-9.5304
H(181)	-2.9454	11.5141	3.721
H(182)	-7.3154	0.7153	11.4487
H(183)	-10.8711	-8.598	2.9471
H(184)	-3.6076	-4.877	3.3249
H(185)	-4.7584	-5.6728	0.6206
H(186)	-4.9678	-6.6308	2.0629
H(187)	-6.1145	-4.6685	3.1741
H(188)	-5.9498	-3.7668	1.6906
H(189)	-7.3863	-7.6203	2.3224
H(190)	-7.8873	-6.4899	3.5769
H(191)	-10.1611	-6.35	2.5799
H(192)	-9.6736	-7.409	1.263
H(193)	-9.8016	-8.2008	4.1052
H(194)	-8.8551	-6.1519	-8.358
H(195)	-7.2747	7.6345	-8.0943
H(196)	-5.8902	11.3721	3.8352
H(197)	-3.9841	12.3624	2.7929
H(198)	-7.6459	2.2569	11.0347
H(199)	-2.2529	-3.8736	-5.2947
C(200)	-3.1241	-3.6715	-4.6816
C(201)	-4.2704	-3.2344	-5.5884
C(202)	-5.6504	-3.3192	-4.9361
S(203)	-7.0415	-2.8364	-6.0184
C(204)	-7.2514	-4.287	-7.1068
C(205)	-8.5845	-4.1183	-7.8339
H(206)	-3.3728	-4.5929	-4.1626
H(207)	-4.0872	-2.2244	-5.937
H(208)	-4.2435	-3.8802	-6.4617
H(209)	-5.8428	-4.3138	-4.5506
H(210)	-5.7192	-2.6333	-4.1014
H(211)	-6.4391	-4.3534	-7.8212
H(212)	-7.2635	-5.1921	-6.5097
H(213)	-9.4184	-4.1266	-7.1487
H(214)	-8.6145	-3.209	-8.4157
H(215)	-1.497	3.8115	-5.3964

C(216)	-2.4014	3.3362	-5.033
C(217)	-3.5047	4.385	-4.9381
C(218)	-4.9101	3.7993	-4.8024
C(219)	-6.2491	5.0359	-4.6714
C(220)	-6.4608	5.6182	-6.3885
C(221)	-7.7664	6.4106	-6.4373
N(222)	-8.0078	6.9955	-7.8143
H(223)	-2.6665	2.5599	-5.7451
H(224)	-3.2983	5.0459	-4.1037
H(225)	-3.4476	4.9869	-5.8408
H(226)	-5.1378	3.128	-5.6224
H(227)	-4.9952	3.2272	-3.8873
H(228)	-5.6288	6.2441	-6.6891
H(229)	-6.5149	4.7673	-7.0584
H(230)	-8.6208	5.7886	-6.2179
H(231)	-7.7556	7.2484	-5.756
H(232)	-8.8768	7.517	-7.842
H(233)	-2.6627	5.5093	0.1072
C(234)	-2.7497	5.1523	1.1265
C(235)	-2.5173	6.2991	2.1161
C(236)	-3.5546	7.4147	1.9275
S(237)	-3.3447	8.7166	3.1964
C(238)	-4.846	9.7142	2.9263
C(239)	-4.9425	10.8619	3.9253
H(240)	-3.7461	4.7495	1.2551
H(241)	-2.5837	5.9071	3.1249
H(242)	-1.5157	6.6963	1.985
H(243)	-3.4665	7.8634	0.9458
H(244)	-4.5566	7.016	2.032
H(245)	-4.8814	10.0903	1.9098
H(246)	-5.7243	9.0996	3.0768
H(247)	-4.819	10.5242	4.9434
H(248)	-3.8763	11.9105	3.6917
H(249)	-1.5676	0.295	6.7457
C(250)	-2.3912	0.7676	6.2215
C(251)	-3.7048	0.2551	6.8027

C(252)	-4.9212	1.1	6.4239
S(253)	-6.5105	0.5127	7.1081
C(254)	-6.4557	1.0682	8.8462
C(255)	-7.866	0.913	9.4134
N(256)	-7.9183	1.2949	10.879
H(257)	-2.2957	1.8394	6.3711
H(258)	-3.8575	-0.772	6.4914
H(259)	-3.5908	0.2455	7.8832
H(260)	-4.7844	2.1367	6.7093
H(261)	-5.0761	1.0799	5.3527
H(262)	-5.7521	0.4753	9.4187
H(263)	-6.1488	2.1073	8.8877
H(264)	-8.5734	1.5526	8.908
H(265)	-8.2123	-0.1084	9.3596
C(266)	-5.0393	-1.2387	-1.093
H(267)	5.8268	-1.6269	2.014
C(268)	-5.6298	-0.9097	0.2761
H(269)	5.8642	-2.5323	-1.5454
C(270)	-4.6967	0.0088	1.0587
H(271)	6.571	-0.4334	0.4627
C(272)	-3.2894	-0.5492	1.158
H(273)	2.6514	1.0781	0.2705
C(274)	-2.809	-1.3871	0.0435
C(275)	-3.6023	-1.676	-0.9916
C(276)	-2.5799	-0.282	2.0851
C(277)	-0.3242	0.2381	-0.4076
C(278)	-0.2304	-1.1059	-0.0583
C(279)	-1.4217	-1.9795	0.152
C(280)	0.794	1.0203	-0.6047
C(281)	2.0649	0.4641	-0.449
C(282)	2.1692	-0.8822	-0.1012
C(283)	1.0331	-1.6521	0.0912
N(284)	3.2165	1.2136	-0.6322
C(285)	4.4826	0.6867	-0.4856
N(286)	4.5753	-0.6528	-0.1418
C(287)	3.4936	-1.5008	0.0658

C(288)	5.9048	-1.2025	0.0118
C(289)	6.5299	-1.7623	-1.0952
C(290)	7.8013	-2.2935	-0.9274
C(291)	8.4206	-2.2642	0.3082
C(292)	7.7769	-1.7028	1.3951
C(293)	6.5051	-1.1621	1.2639
C(294)	5.8036	-0.5505	2.4528
C(295)	5.8549	-1.7963	-2.4453
O(296)	-3.1058	-2.3508	-2.0321
O(297)	-1.2948	-3.1409	0.3943
O(298)	5.4635	1.3507	-0.6477
O(299)	3.6528	-2.6471	0.357
C(300)	3.1163	2.6246	-0.9882
H(301)	-5.093	-0.3776	-1.7573
H(302)	-5.6116	-2.033	-1.5667
H(303)	-6.6044	-0.4499	0.1568
H(304)	-5.7772	-1.8326	0.8285
H(305)	-4.6253	0.9777	0.5665
H(306)	-5.0537	0.1876	2.0647
H(307)	-1.289	0.6915	-0.534
H(308)	0.6704	2.0496	-0.871
H(309)	1.145	-2.6838	0.3599
H(310)	8.3058	-2.7325	-1.7695
H(311)	9.4057	-2.6803	0.4244
H(312)	8.2625	-1.6835	2.3544
H(313)	6.4278	-0.6135	3.3356
H(314)	5.5792	0.4972	2.2802
H(315)	4.8728	-1.0646	2.6678
H(316)	4.9249	-2.3536	-2.4059
H(317)	5.6345	-0.7945	-2.7994
H(318)	6.4951	-2.2723	-3.1779
H(319)	-3.7809	-2.5999	-2.6481
H(320)	4.11	3.0219	-1.0763
H(321)	2.6002	2.7372	-1.9335
H(322)	2.5796	3.1674	-0.2201

11. ^{1}H NMR titration experiments between benquitrione and AP5A

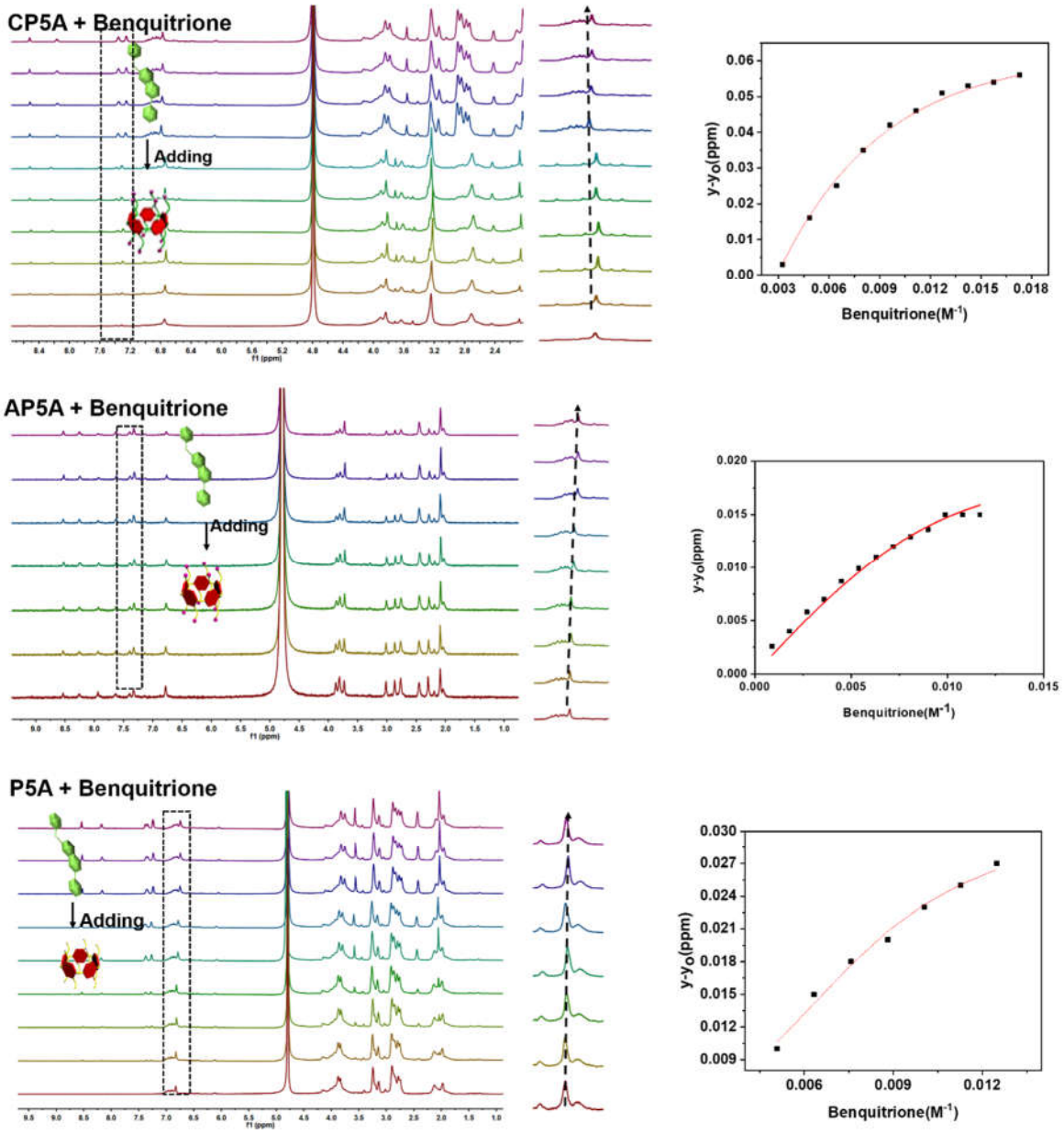

Figure S10. ^{1}H NMR titration of interaction between benquitrione and CP5A, AP5A and P5A (600 MHZ, D_2O, 298 K). The constant concentration of the fixed AP5A (1.0×10^{-5} mol / L) the gradual drip of benquitrione (1.0×10^{-3} mol / L), the apparent shift of hydrogen on the benzene ring in AP5A indicates that benquitrione can self-assemble into the AP5A cavity and has a stable interaction.

12. The construction of silicon surface

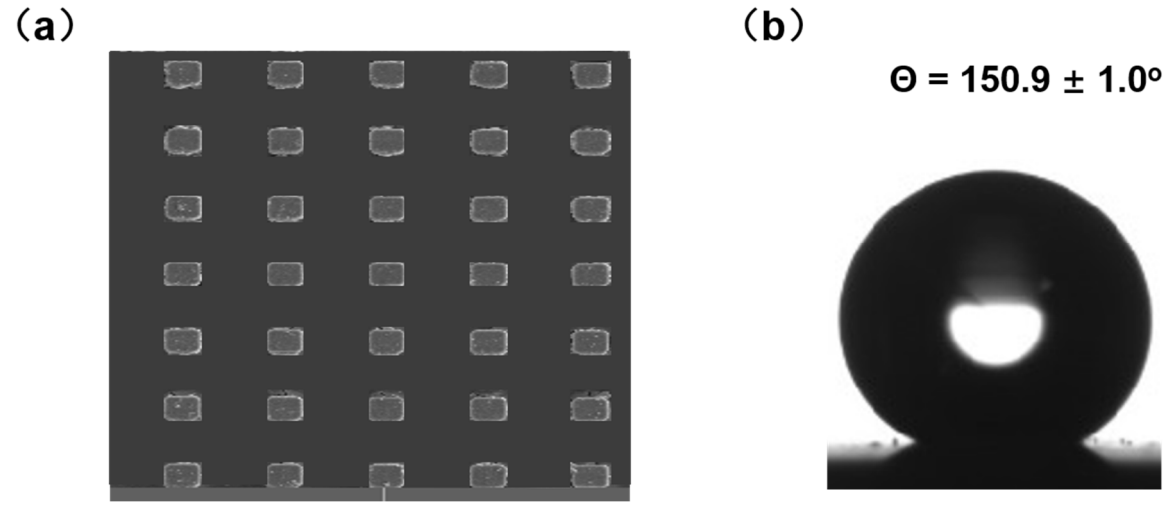

Figure S11. a) Construction of biomimetic superhydrophobic Interface. Silicon surfaces were kept dipped in acidic $KMnO_4$ overnight and washed using DI water. Then the silicon surface was kept dipped in 0.01 % NaOH and HNO_3 for 10 min and 2 min respectively. Finally, surfaces were dipped in a triethoxy (octyl) silane dissolved in toluene for 8 h to modify the surface to make it superhydrophobic. At each step silicon surfaces were dried using N_2 (g); b) The contact angle of pure water droplets on the modified silicon is 150.9 ± 1°, indicating that the surface is superhydrophobic.

13. Dynamic spreading area on superhydrophobic silicon surface

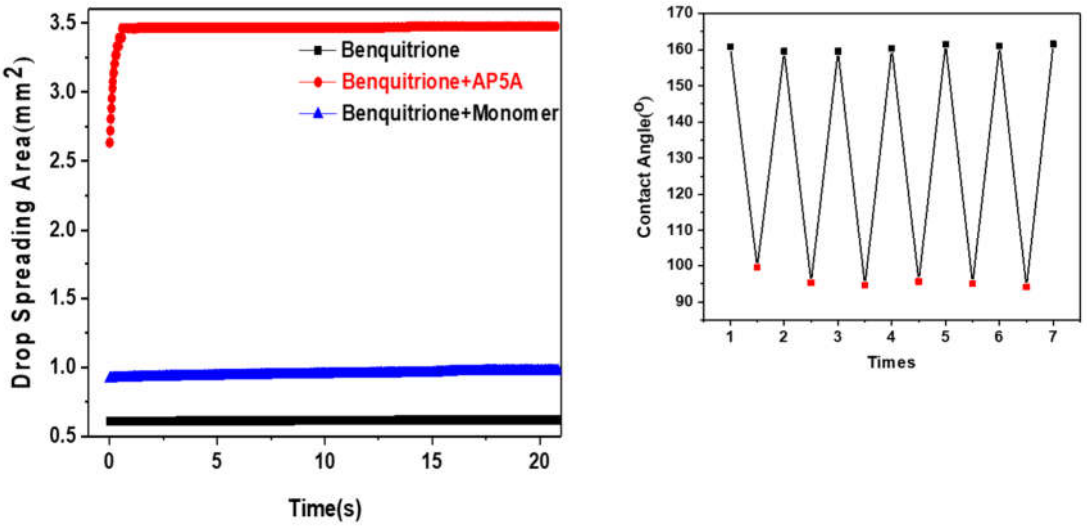

Figure S12. Dynamic spreading area and cycling process of different droplets (1.0×10^{-3} mol / L, 3 μL) on superhydrophobic silicon surface. The expanded area of the benquitrione and its monomers remained stable over time. However, the spreading area of the complex increases rapidly within 1 s and then slowly changes to stabilize, indicating that the spreading of benquitrione can be promoted by AP5A. At the same time, in order to reduce the accidental error, seven experiments were performed on the same superhydrophobic silicon surface, and the same results were obtained.

14. Effect of concentration on spreading area of different droplets

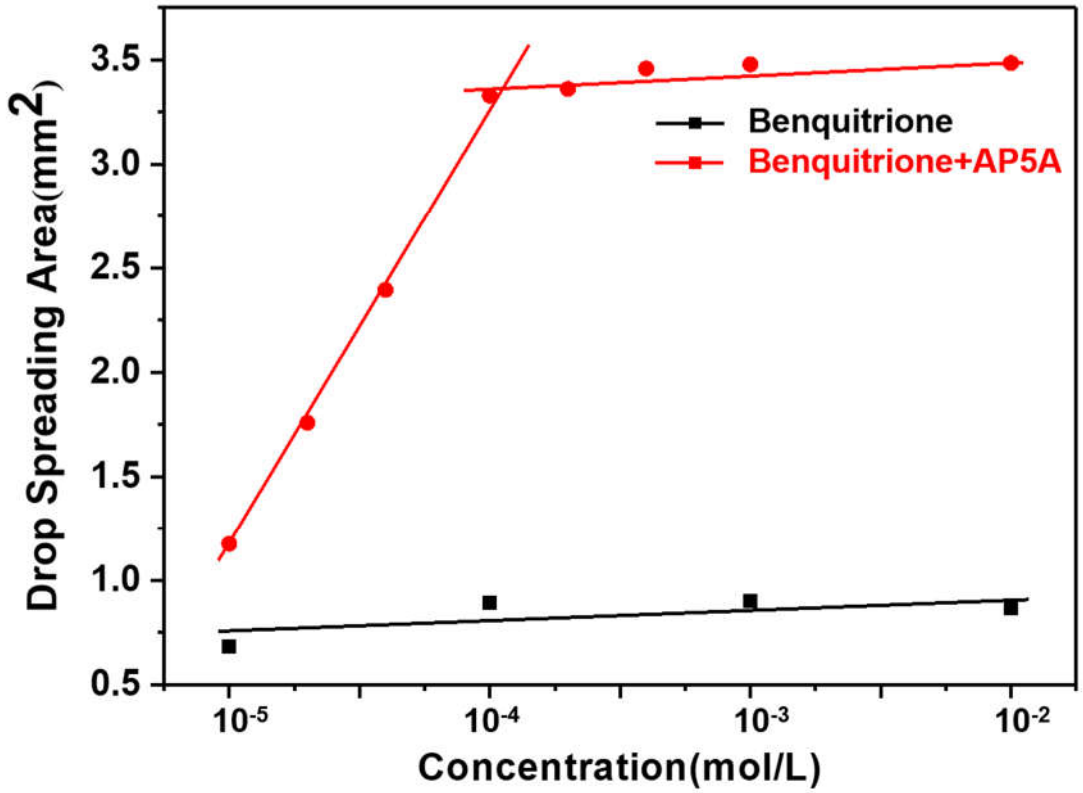

Figure S13. The spreading area of different concentrations of benquitrione, benquitrione and AP5A complex droplets (1.0×10^{-3} mol / L, 3 μL). The spreading area of droplet benquitrione added with AP5A increased rapidly with the change of concentration. At the concentration 2.0×10^{-4} mol / L, the spreading area of droplet benquitrione reached the maximum, and then the maximum spreading area did not change with the increase of concentration.

15. SEM imaging of benquitrione and complex

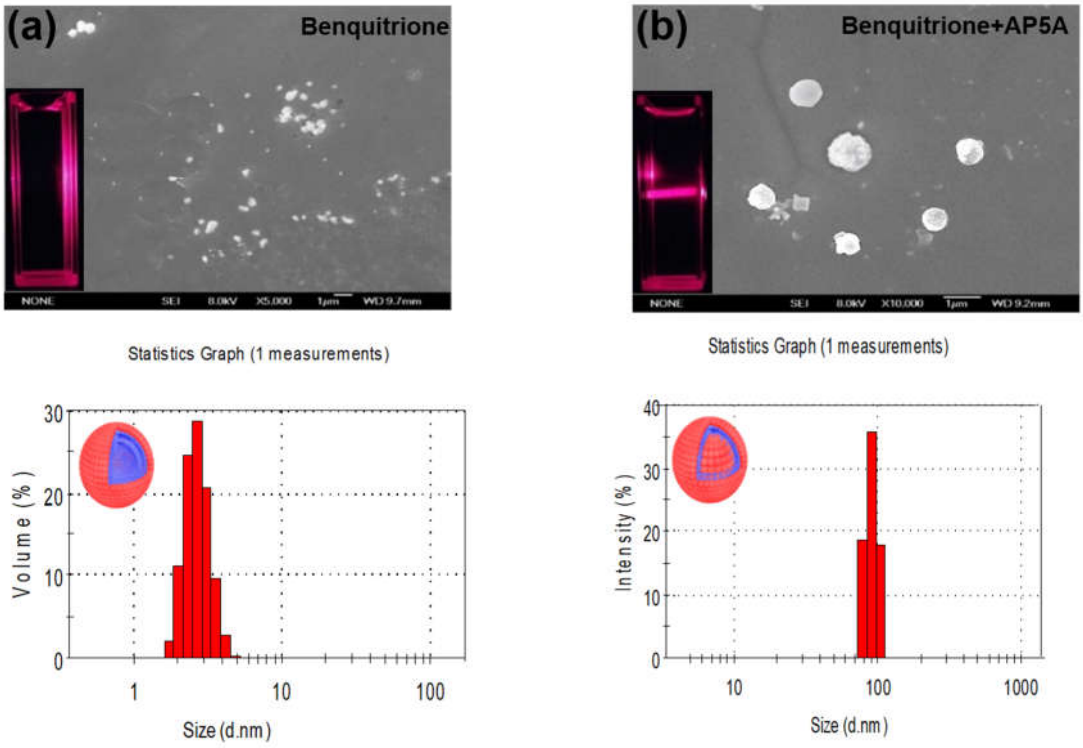

Figure S14. a) SEM imaging of benquitrione and particle size of benquitrione. In aqueous solution, pesticide benquitrione do not aggregate and are scattered in the solution with a particle size of about 5 nm; b) SEM imaging and particle size of complexes. It was found by SEM that aggregates were formed in the solution, which indicated that the complex of benquitrione and AP5A could spontaneously aggregate to form vesicles. Tyndall effect also showed that benquitrione solution alone did not aggregate, but the complex solution did.

16. Contact angle imaging on the surface of bamboo leaves

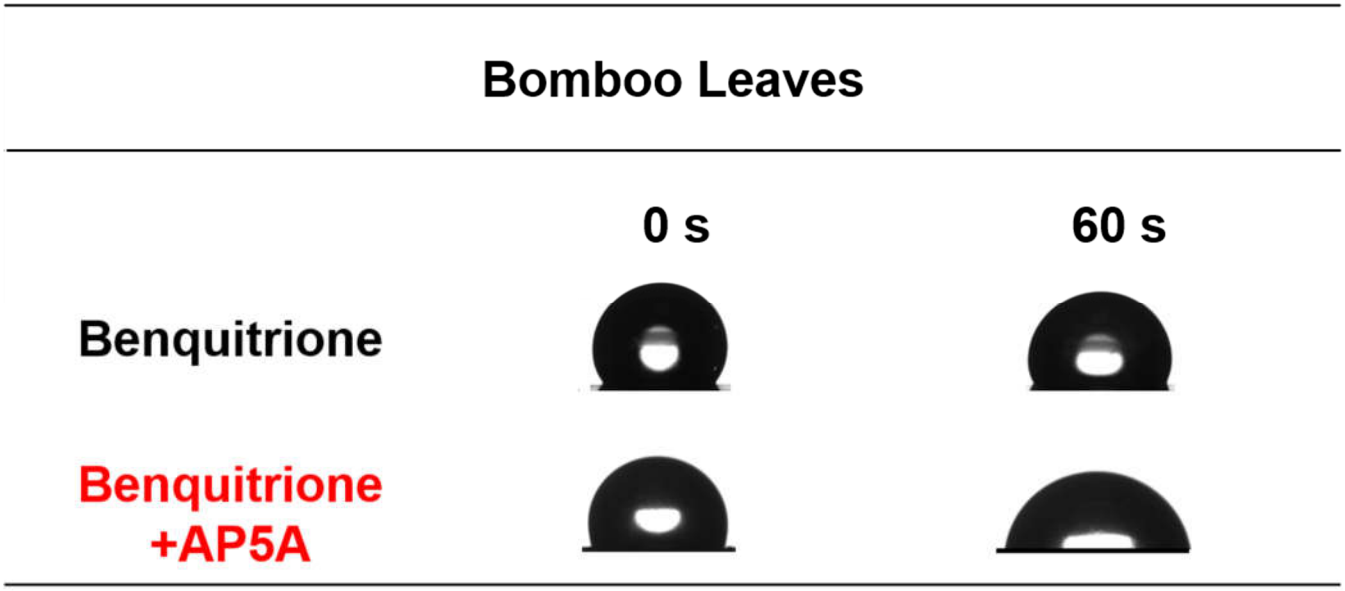

Figure S15. The change of contact angle of benquitrione and complex between benquitrione and AP5A on bamboo leaves. After contact for 60 s, the spreading imaging of benquitrione droplets did not change, and the spreading area of droplet complexes increased significantly.

17. The spreading area on bamboo leaves

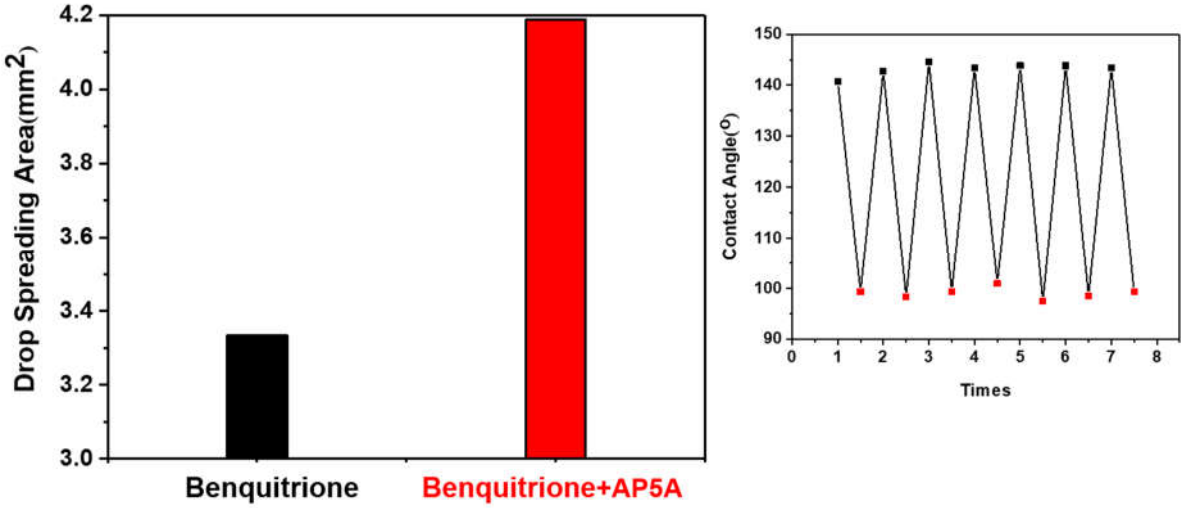

Figure S16. The spreading area of benquitrione and complex between benquitrione and AP5A. The spreading area was calculated by using the contact angle measured many times, and the experiment was repeated seven times. The spreading area of the complex is 1.4 times larger than that of the benquitrione solution.

18. Contact angle imaging on the surface of cotton leaves

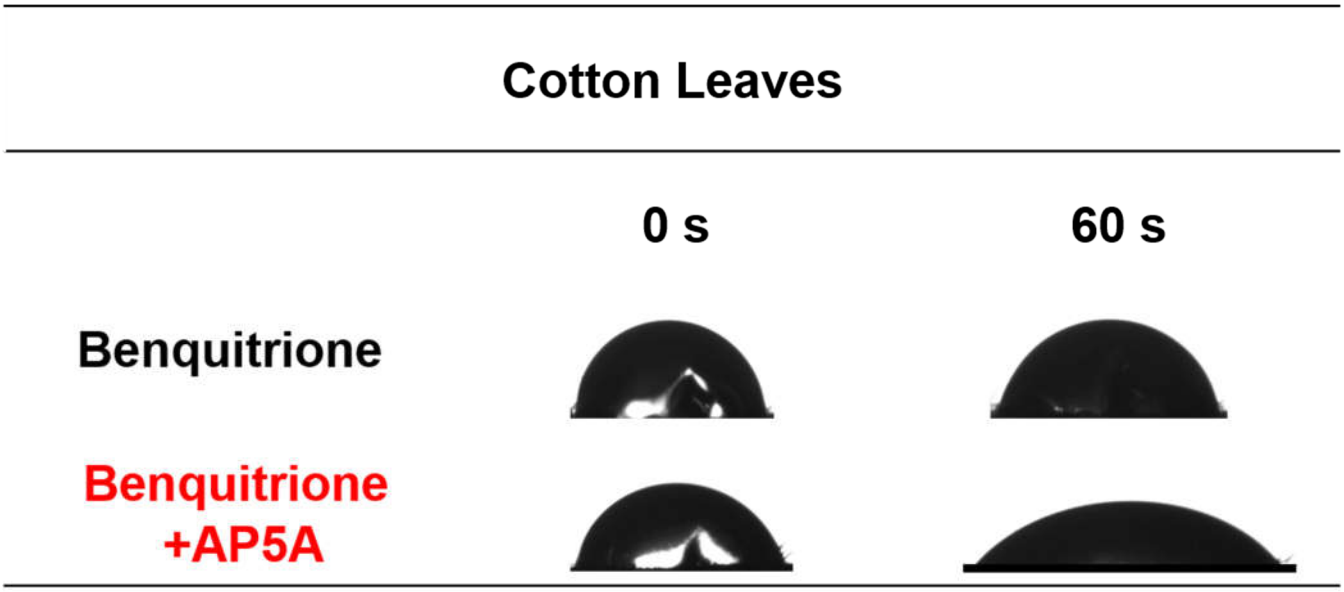

Figure S17. The change of contact angle of benquitrione and complex between benquitrione and AP5A on cotton leaves. After contact for 60 s, the spreading imaging of benquitrione droplet did not change, and the spreading area of droplet complexes increased significantly.

19. The spreading area on bamboo leaves

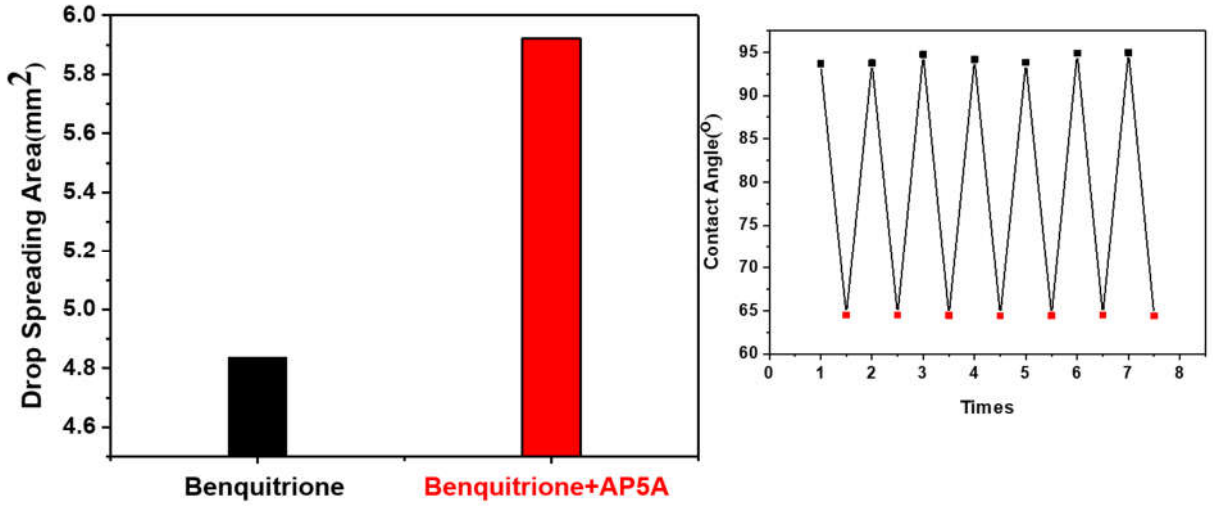

Figure S18. The spreading area of benquitrione and complex between benquitrione and AP5A. The spreading area was calculated by using the contact angle measured many times, and the experiment was repeated seven times in the same position. The spreading area of the complex is 1.3 times larger than that of the benquitrione solution.

20. Inhibition of *At*HPPD

Buffer is HEPES (40 mM, pH = 7.0), substrate HPPA concentration is 50 mM, *At*HPPD is 14 nM, cofactor sodium ascorbate is 2 mM, ferrous sulfate is 100 mM, coupling enzyme HGD is sufficient. The reaction mechanism for the competitive slow-binding inhibitors.

$$\begin{array}{ccccc} & & I & & \\ & & + & & \\ S + E & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & ES & \xrightarrow{k_2} & E + P \\ & & \Big\Downarrow{\scriptstyle k_{+0}} \; {\scriptstyle k_{-0}} & & \\ & & EI & & \end{array}$$

Where *S, E, I* and *P* represent the substrate, enzyme, inhibitor and product, respectively. According to the substrate reaction kinetic theory, the accumulation of product with time can be expressed by equation (1):

$$[P] = v_s t + \frac{v_0 - v_s}{k_{obs}}\left(1 - e^{-k_{obs}t}\right) \tag{1}$$

where v_0 and v_s are the initial and steady-state velocities of the reaction in the presence of inhibitor. k_{obs} is the observed first order rate constant, which can be generated against inhibitor concentration.

$$k_{obs} = A[I]_0 + B \tag{2}$$

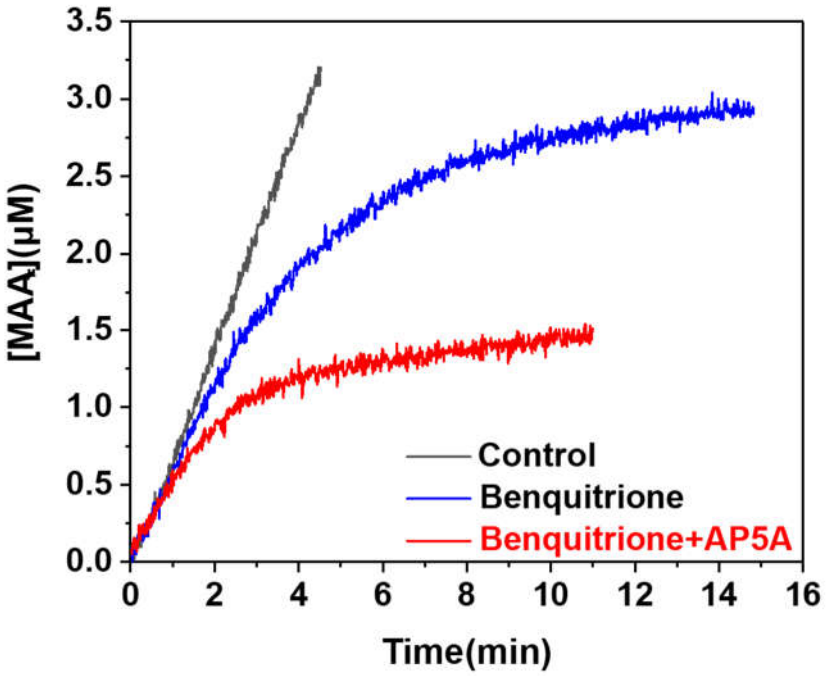

Figure S19. Inhibition of *At*HPPD (14.0 nM) by benquitrione and complexes (1.0 μM). It can be seen from the diagram that the reaction rate of the blank control group is 0.721 ± 0.0021 μM / min, the apparent rate constant of benquitrione was k_{obs} = 0.2289 ± 0.003 min^{-1}, steady state rate is v_s = 0.0507 μM / min, and the apparent rate constant of complex was k_{obs} = 0.5648 ± 0.0102 min^{-1}, steady state rate is v_s = 0.0347 μM / min. According to the steady-state apparent rate, the inhibition rate of benquitrione can be calculated as 92.9 %, and the inhibition rate of the complex is 95.2 %, which indicates that AP5A did not significantly change the activity of benquitrione within the error tolerance.

21. Weeding- foliage effect test

A certain amount of the original drug was weighed using an analytical balance (0.10 mg), and dissolved in a DMF containing 1% Tween-80 emulsifier to prepare a mother liquor of 0.5-1%, and then diluted with distilled water for use.

Post-emergence stem and leaf spray: take 7cm inner diameter paper cup, install composite soil (garden soil: seedling substrate, 1:2, v / v) to 3 / 4, directly weed, cover soil 0.2 cm, wait until length 4-5 leaf period alternate. The new compound was applied to the greenhouse after the application of 150 g. a. I / ha; benquitrionee at a dose of 150 g. a. I / ha in the automatic spray tower. After the leaf foliar solution was dried, it was transferred to the greenhouse for cultivation (25 degrees-28 degrees, humidity 70 %). The results of the survey every day.

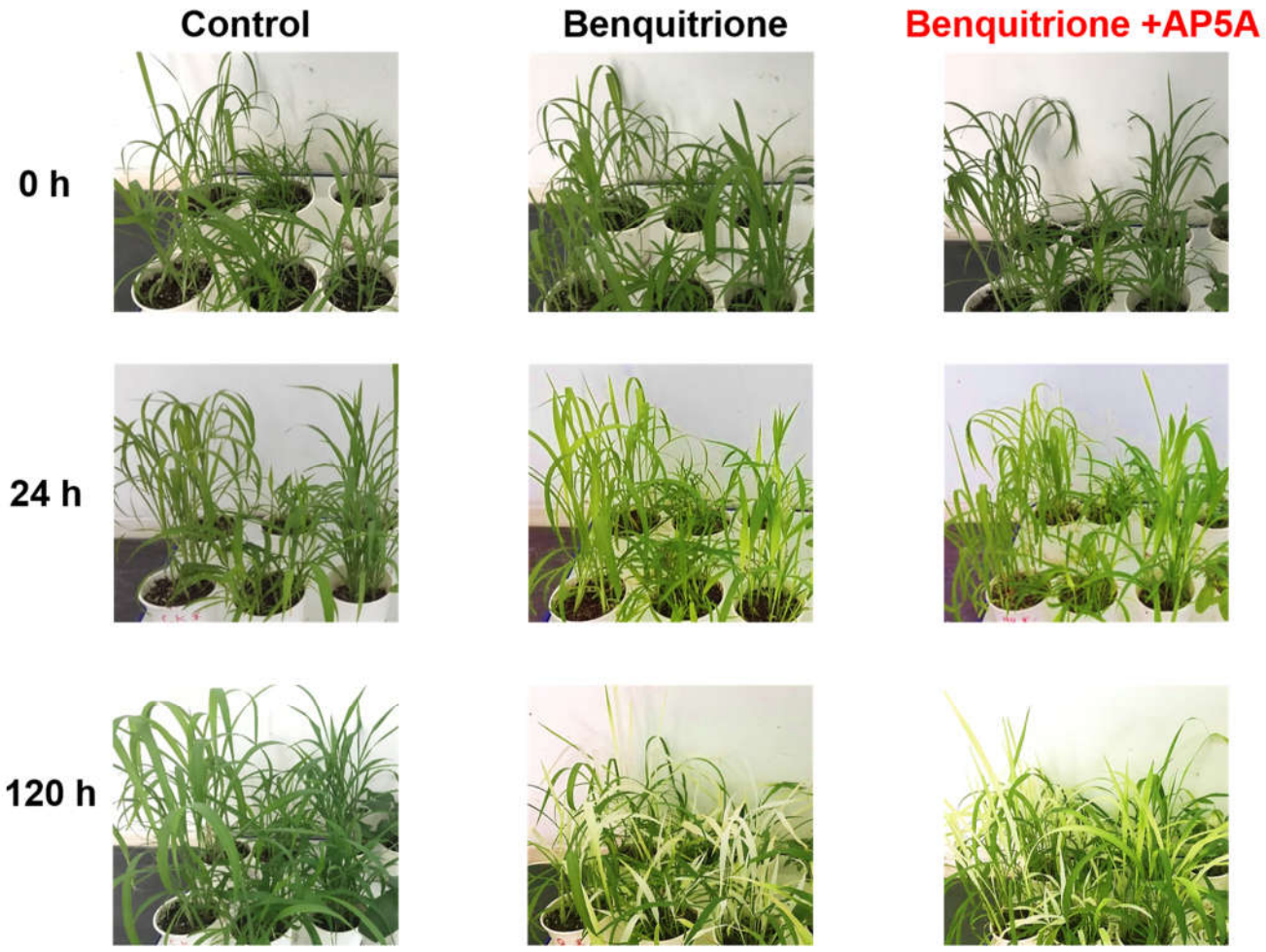

Figure S20. Herbicidal effect of benquitrione and its complexes under natural light. The control (water), benquitrione and combination preparations were applied to the leaves in a natural environment and monitored. After 1 day, the benquitrione and the complex weeds began to whiten, and after 5 days, they began to die. The above results indicate that the herbicidal activity of the pesticide benquitrione after the addition of AP5A is not lowered.

22. Weeding-chenopodium album L. effect test

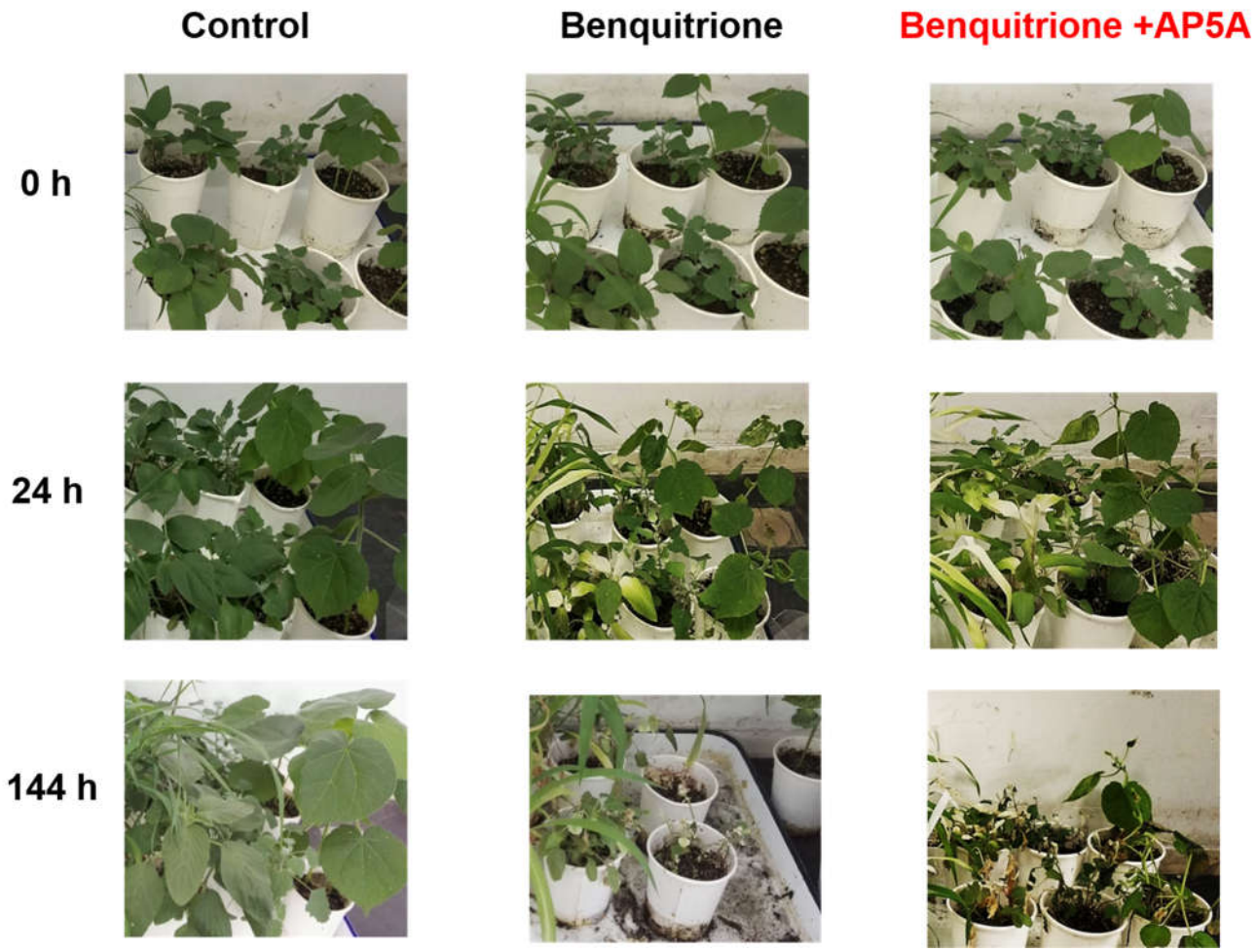

Figure S21. Herbicidal effect of benquitrione and its complexes under natural light. The control (water), benquitrione and combination preparations were applied to the leaves in a natural environment and monitored. After 1 day, the benquitrione and the complex weeds began to whiten and part die, and almost completely died after 6 days. The above results indicate that the herbicidal activity of the pesticide benquitrione after the addition of AP5A is not lowered.

23. Construction of bionic superhydrophobic surface

Fabrication of the Si surface: The silicon wafer was used directly as the smooth substrate, the structured silicon substrate was fabricated by the combination of the photolithography and inductively coupling plasma (ICP) deep etching technique. The photolithography and ICP technique were used to obtain the patterned silicon micropillar structure on silicon wafer. A rough surface introduced geometrical structures with patterned square pillars on a flat silicon wafer, 20 μm high, 4 μm long and with spacing of 6 μm between the silicon pillars.

The click reaction to fabricate the triethyloctylsilane silicon substrates: silicon surfaces were kept dipped in acidic $KMnO_4$ overnight and washed using DI water. Then the silicon surface was kept dipped in 0.01 % NaOH and HNO_3 for 10 and 2 min respectively. Finally surfaces were dipped in a triethoxy(octyl)silane dissolved in toluene for 8 hours to modify the surface to make it hydrophobic. At each step silicon surfaces were dried using N_2. [36]

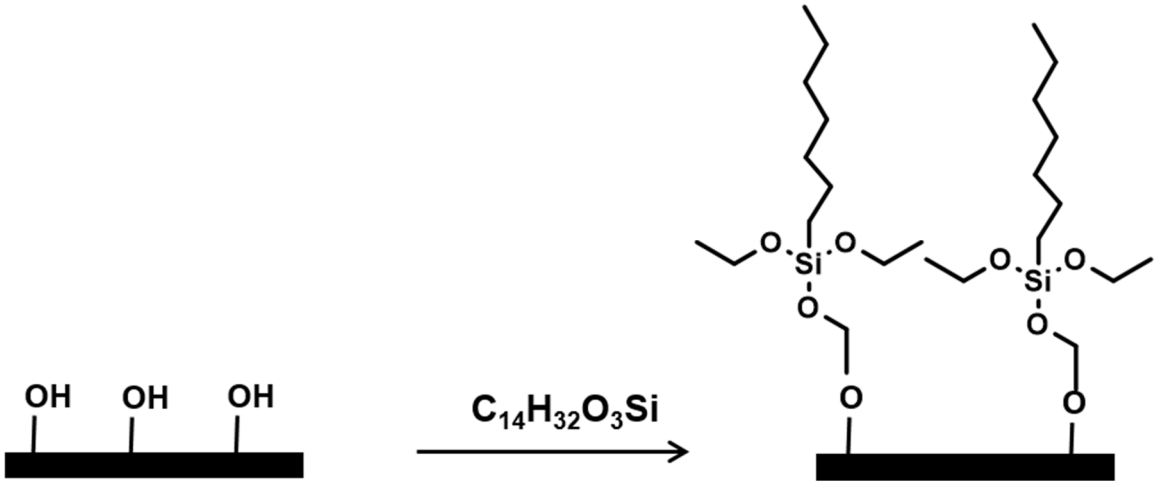

Figure S22. Construction of bionic superhydrophobic surface.

24. Microstructure of plant leaf surface

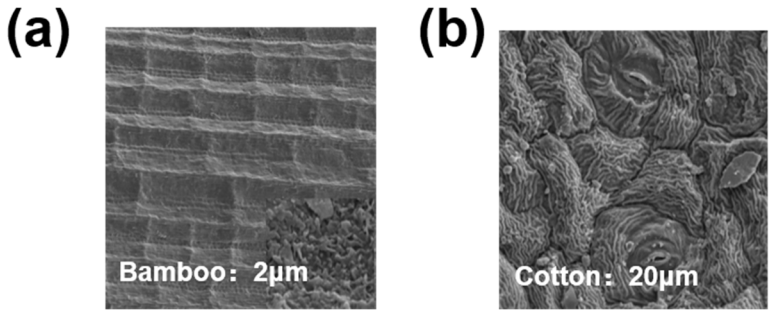

Figure S23. Construction of bionic superhydrophobic surface. a) The construction of bomboo leave surface. SEM showed that the morphological characteristics of bamboo leaves were the hierarchical 3-D structure constructed by the combination of micron and nano-structure. It is found that bamboo leaves have sub-millimeter-scale-grooves and patterned arrays. From the partially enlarged image, it was observed that cylindrical conical micropore superimposed by densely arranged waxy nanosheets randomly distributes on the surface of plants, and the wax layer of the cuticle layer of plants covers the surface; b) The construction of cotton leave surface. The surface of cotton has a relatively smooth 2-D wax layer, which has cuticle and randomly distributed oval stomata.

25. Spreading on bomboo and cotton leaves

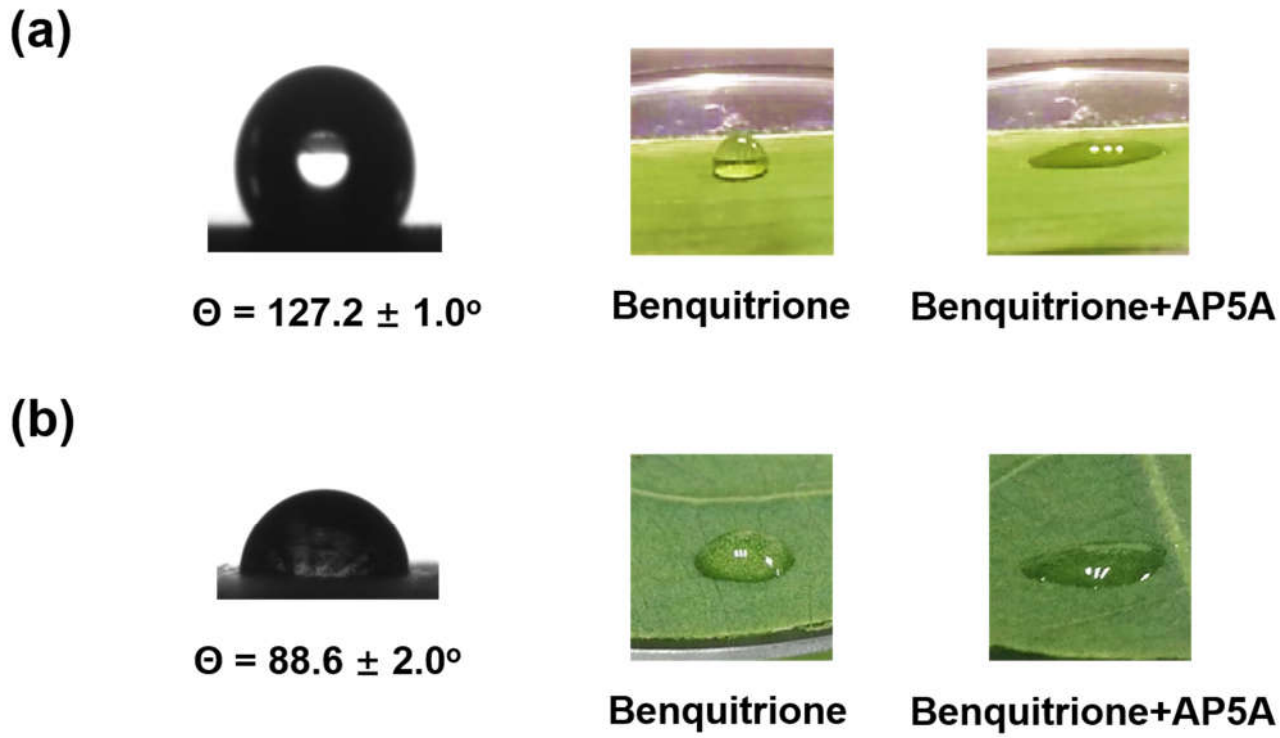

Figure S24. a) The contact angle of bomboo leave surface. Contact angle of water droplet on bamboo leaves, image of benquitrione droplets and benquitrione + AP5A on bamboo leaves. Contact Angle was 127.2 ± 1.0o and benquitrione + AP5A droplets in bamboo leaf surface spread out completely; b) The contact angle of cotton leave surface. Contact angle of water droplet on cotton leaf, image of benquitrione droplet and benquitrione + AP5A on cotton leaves. The contact angle was 88.6 ± 2.0o. Part benquitrione droplet spreading, benquitrione + AP5A droplets spread out completely.

26. Spreading of droplets on superhydrophobic silicon surface

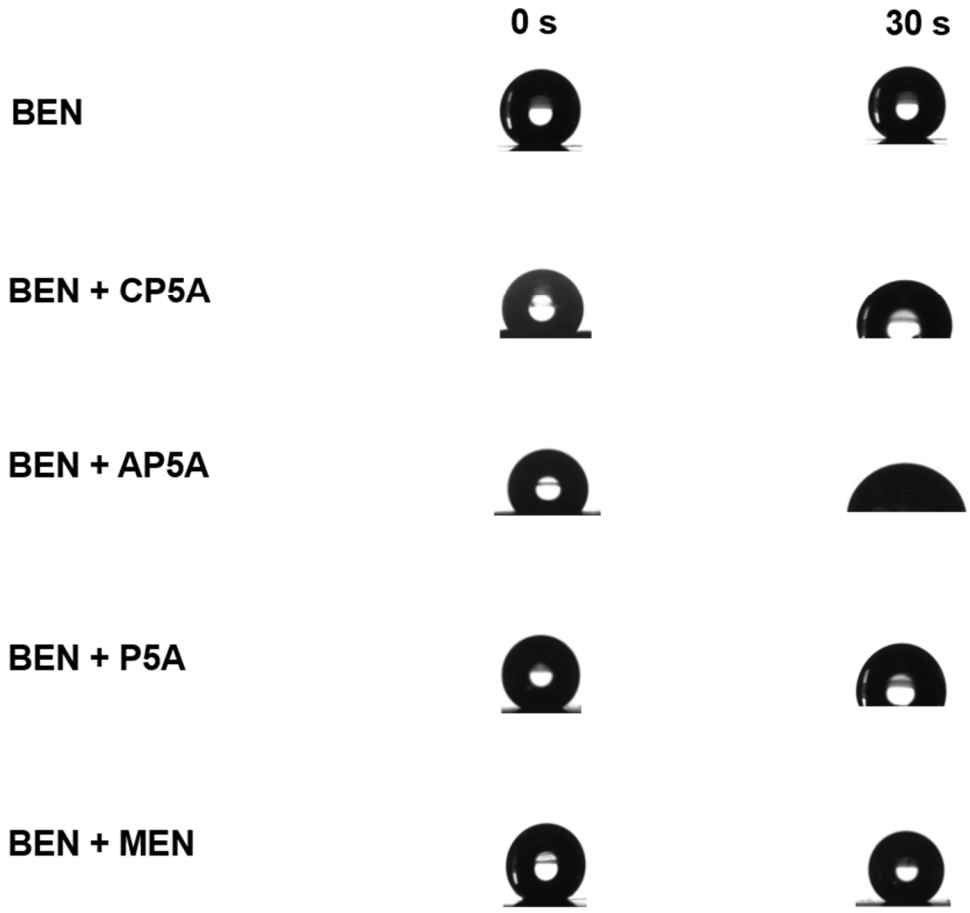

Figure S25. The change of the contact angle of BEN, BEN + CP5A, BEN + AP5A, BEN + P5A and BEN + MER with 30 s on superhydrophobic silicon surface.