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Supporting Information

for

Electrochemical and spectroscopic properties of twisted dibenzo[*g*,*p*]chrysene derivatives

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Figures S1–S3, Tables S1–S6, general, experimental procedure, and cartesian coordinates of optimized structures obtained based on the theoretical calculation

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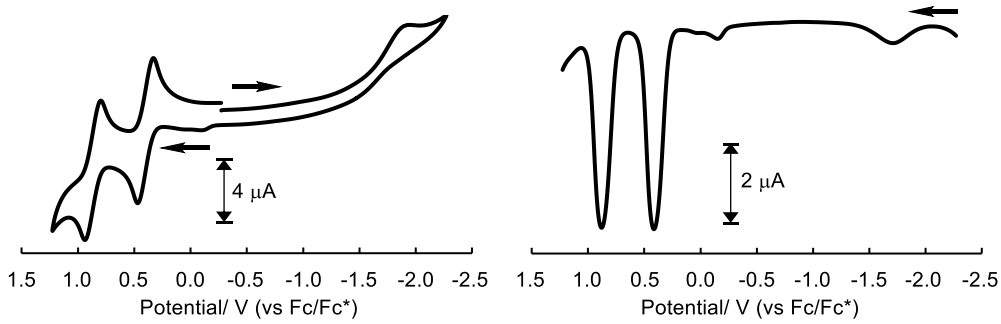
1. Figures (S1–S3)

DBC-SMe



DBC-S(O)$_2$Me

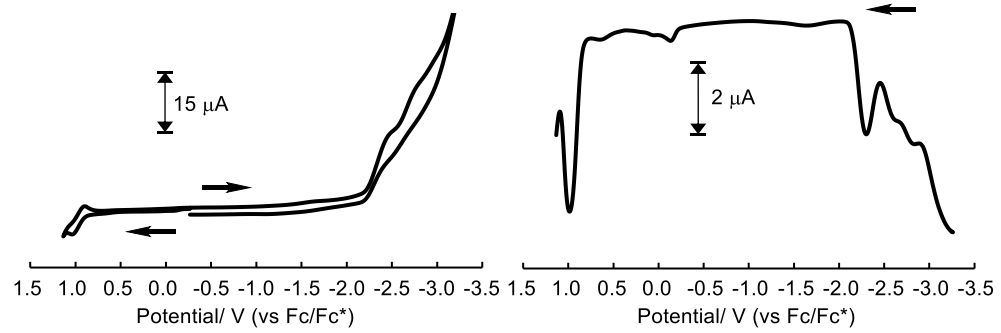


Figure S1. CVs and SWVs of **DBC-SMe** and **DBC-S(O)$_2$Me** in CH_2Cl_2 (≈1.0×10^{-3} M, see below for details) including 5.0×10^{-2} M Bu_4NBF_4 as a supporting electrolyte under Ar at 25 °C (working electrode: Pt, scan rate: 100 mV/s and 40 mV/s for CV and SWV measurements, respectively).

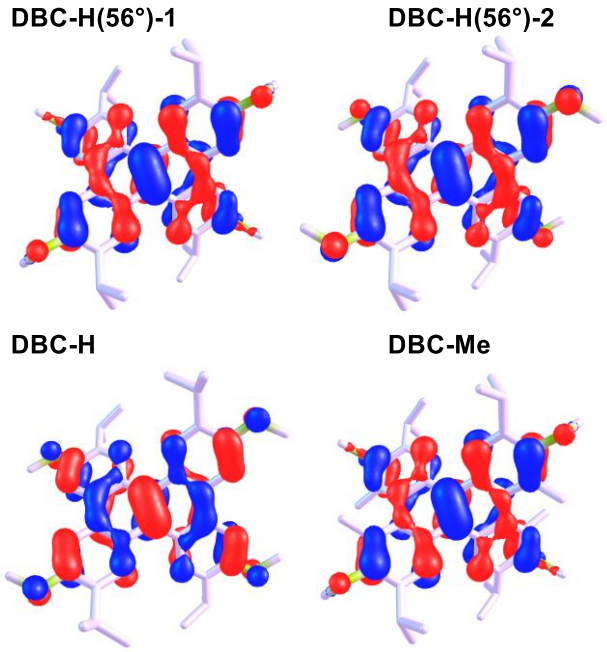


Figure S2. Orbital drawings of HOMO for DBC derivatives.

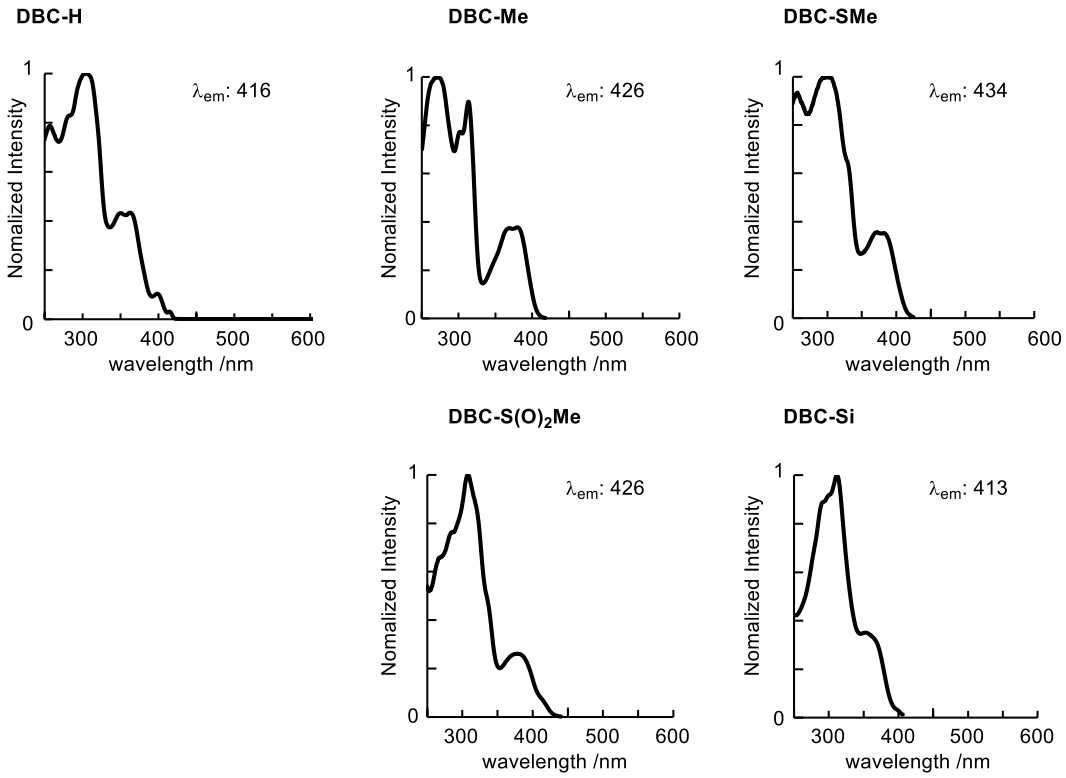


Figure S3. Excited spectra for DBC derivatives in CH_2Cl_2.

Table S1. Wavelengths and oscillator strengths (*f*) for **DBC-H** estimated by TD-DFT calculation [TD-B3LYP-D3/6-31G(d,p)// B3LYP/6-31G(d,p)]

Excited state	Wavelength (nm)	*f*	Transition ($\psi_{xxx} \rightarrow \psi_{yyy}$)					
1	375.36	0.0409	165 → 167	-0.33401	166 → 168	0.61777		
2	367.64	0.1474	165 → 168	0.22931	166 → 167 (HOMO→LUMO)	0.66346		
3	348.78	0.0000	164 → 167	-0.18876	166 → 169	0.67616		
4	321.69	0.4225	165 → 167	0.57466	166 → 168	0.31408	166 → 170	-0.24859
5	301.66	0.4664	164 → 169	-0.11143	165 → 168	0.65429	166 → 167 (HOMO→LUMO)	-0.21024

Table S2. Wavelengths and oscillator strengths (*f*) for **DBC-Me** estimated by TD-DFT calculation [TD-B3LYP-D3/6-31G(d,p)// B3LYP/6-31G(d,p)]

Excited state	Wavelength (nm)	*f*	Transition ($\psi_{xxx} \rightarrow \psi_{yyy}$)					
1	382.98	0.2250	181 → 184	0.14522	182 →183 (HOMO→LUMO)	0.68676		
2	364.35	0.0181	181 → 183	-0.40652	182 → 184	0.57291		
3	344.69	0.0000	180 → 183	-0.32512	182 → 185	0.61825		
4	320.20	0.4413	181 → 183	0.55590	182 → 184	0.39632	182 → 186	-0.14875
5	307.82	0.0000	180 → 183	0.61328	182 → 185	0.32188		

Table S3. Wavelengths and oscillator strengths (*f*) for **DBC-SMe** estimated by TD-DFT calculation [TD-B3LYP-D3/6-31G(d,p)// B3LYP/6-31G(d,p)]

Excited state	Wavelength (nm)	*f*	Transition ($\psi_{xxx} \rightarrow \psi_{yyy}$)					
1	386.11	0.1776	212 → 216	0.15435	214 → 215 (HOMO→LUMO)	0.68395		
2	373.77	0.0382	212 → 215	-0.33988	214 → 216	0.61244		
3	354.45	0.0000	208 → 215	-0.21817	210 → 215	-0.12908	214 → 217	0.64660
4	341.43	0.0041	213 → 215	0.69332				
5	328.47	0.3898	211 → 216	0.10352	212 → 215	0.58018	214 → 216	0.32907
					214 → 218	0.18299		

Table S4. Wavelengths and oscillator strengths (*f*) for **DBC-Br** estimated by TD-DFT calculation [TD-B3LYP-D3/6-31G(d,p)// B3LYP/6-31G(d,p)]

Excited state	Wavelength (nm)	*f*	Transition ($\psi_{xxx} \rightarrow \psi_{yyy}$)					
1	393.50	0.1852	233 → 236	0.14200	234 → 235 (HOMO→LUMO)	0.68627		
2	378.99	0.0344	233 → 235	-0.33512	234 → 236	0.61613		
3	362.28	0.0000	232 → 235	0.27025	234 → 237	0.64431		
4	332.41	0.3147	233 → 235	0.58566	234 → 236	0.32549	234 → 238	0.20022
5	320.89	0.0000	232 → 235	0.63722	234 → 237	-0.27031		

Table S5. Wavelengths and oscillator strengths (*f*) for **DBC-S(O)$_2$Me** estimated by TD-DFT calculation [TD-B3LYP-D3/6-31G(d,p)// B3LYP/6-31G(d,p)]

Excited state	Wavelength (nm)	*f*	Transition ($\psi_{xxx} \rightarrow \psi_{yyy}$)					
1	393.30	0.1311	245 → 248	0.18016	246 → 247 (HOMO→LUMO)	0.67649		
2	391.34	0.0269	245 → 247	-0.30004	246 → 248	0.63429		
3	375.53	0.0004	244 → 247	0.19897	246 → 249	0.67199		
4	341.34	0.3149	245 → 247	0.60776	246 → 248	0.29604	246 → 251	0.18560
5	318.88	0.0003	242 → 248	-0.11521	244 → 247	0.65664	246 → 249	-0.19851

Table S6. Wavelengths and oscillator strengths (*f*) for **DBC-Si** estimated by TD-DFT calculation [TD-B3LYP-D3/6-31G(d,p)// B3LYP/6-31G(d,p)]

Excited state	Wavelength (nm)	*f*	Transition ($\psi_{xxx} \rightarrow \psi_{yyy}$)					
1	377.71	0.1275	195 → 198	0.15828	196 → 197 (HOMO→LUMO)	0.66980		
2	373.16	0.0094	195 → 197	-0.36578	196 → 198	0.58965		
3	363.25	0.0013	194 → 197	-0.17595	196 → 199	0.67802		
4	336.34	0.1321	195 → 197	0.46872	195 → 198	-0.10438	196 → 198	0.34027
			196 → 200	0.37335				
5	316.65	0.0159	194 → 197	0.34173	195 → 199	0.58542	196 → 199	0.11324

3. General

All the DBC derivatives reported here were synthesized according to our previous paper [S1]. The electrochemical studies were performed on a BAS ALS842D voltammetry analyzer. Absorption spectra were measured on a JASCO V-770 spectrometer using a quartz cuvette (1 cm square). Emission spectra were measured on a JASCO FP-8500 spectrometer. Concentration for the spectroscopic measurements is as follows, **DBC-H**: 1.03×10^{-5} M, **DBC-Me**: 3.97×10^{-6} M, **DBC-SMe**: 4.00×10^{-6} M, **DBC-Br**: 3.98×10^{-6} M, **DBC-S(O)$_2$Me**: 4.00×10^{-6} M, and **DBC-Si**: 1.00×10^{-5} M. Quantum yield was measured based on the absolute quantum yield method using an integrating sphere (JASCO ILF-835). All calculations were conducted using a Gaussian 16 suite program (G16RevC.01)[S2]. In the present study, the optimization for **DBC-H(56°)-1** and **DBC-H(56°)-2** was performed at the B3LYP/6-31G(d,p) level of theory (the calculation for other DBC derivatives were reported in reference [S1]). Harmonic vibration frequency analysis was conducted with the optimized structures at the same level of theory to verify all stationary points as local minima (with no imaginary frequency). TD-DFT calculations for **DBC-H**, **DBC-Me**, **DBC-SMe**, **DBC-Br**, **DBC-S(O)$_2$Me**, and **DBC-Si** based on B3LYP-D3/6-31G(d,p) were performed using the optimized structures based on B3LYP-D3/6-31G(d,p). See also reference [S1] for the DFT calculation of **DBC-H**, **DBC-Me**, **DBC-SMe**, **DBC-Br**, **DBC-S(O)$_2$Me**, and **DBC-Si**.

References

S1. Kamiguchi, S.; Akasaka, R.; Yoshida, N.; Imai, T.; Yamaoka, Y.; Amaya, T.; Iwasawa, T. *Tetrahedron Lett.*, **2022**, *92*, 153664.

S2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

4. Experimental procedure

Electrochemical experiments: The CVs and SWVs and were measured in CH_2Cl_2 containing 5.0×10^{-2} M NBu_4BF_4 as a supporting electrolyte under argon at room temperature with a three-electrode system consisting of a platinum working electrode (BAS), a platinum auxiliary electrode (BAS), and an Ag/AgCl (0.01 M) reference electrode (BAS) at 100 mV/s for CV and 40 mV/s for SWV scan rates. Concentration of DBC derivatives is as follows, **DBC-H**: 1.00×10^{-3} M, **DBC-Me**: 1.00×10^{-3} M, **DBC-SMe**: 0.99×10^{-3} M, **DBC-Br**: 0.97×10^{-3} M, **DBC-S(O)$_2$Me**: 1.00×10^{-3} M, and **DBC-Si**: 1.00×10^{-3} M. Redox potentials are given vs Fc/Fc^+.

5. Cartesian coordinates of optimized structures

DBC-H(56°)-1, optimized at the B3LYP/6-31G(d,p) level of theory.

	Coordinates (Angstroms)		
Atomic Type	X	Y	Z
8	-4.645495	-2.786450	2.335174
8	4.485653	-3.043348	-2.415000
8	4.645495	2.786450	2.335174
8	-4.485653	3.043348	-2.415000
6	1.128883	-2.675016	-1.019320
6	2.489014	0.573785	0.305220
6	1.281584	2.604148	0.940113
6	1.281584	1.335774	0.326084
6	2.450967	-0.715770	-0.395075
6	1.200836	-1.408723	-0.408823
6	0.020441	0.695464	-0.040961
6	-0.020441	-0.695464	-0.040961
6	2.223159	-3.278581	-1.629049
6	3.539014	-1.256248	-1.130522
6	3.562065	2.336408	1.591056
6	2.411041	3.144066	1.542292
6	3.418759	-2.540683	-1.681392
6	-3.609720	-1.049532	1.039181
6	-2.450967	0.715770	-0.395075

6	3.609720	1.049532	1.039181
6	-3.562065	-2.336408	1.591056
6	-1.281584	-1.335774	0.326084
6	-2.489014	-0.573785	0.305220
6	-1.281584	-2.604148	0.940113
6	-3.418759	2.540683	-1.681392
6	-1.128883	2.675016	-1.019320
6	-1.200836	1.408723	-0.408823
6	2.098524	-4.638888	-2.304502
6	-3.539014	1.256248	-1.130522
6	-2.223159	3.278581	-1.629049
6	2.001023	4.298759	3.743524
6	2.384602	4.488021	2.261636
6	-2.411041	-3.144066	1.542292
6	1.089604	-4.605916	-3.468243
6	-2.384602	-4.488021	2.261636
6	-2.098524	4.638888	-2.304502
6	-5.704455	-3.353651	1.566543
6	5.469559	-3.724286	-1.639834
6	1.742646	-5.747537	-1.296680
6	5.704455	3.353651	1.566543
6	1.479183	5.529007	1.586050
6	-1.742646	5.747537	-1.296680
6	-5.469559	3.724286	-1.639834
6	-1.089604	4.605916	-3.468243
6	-1.479183	-5.529007	1.586050
6	-2.001023	-4.298759	3.743524
1	0.166290	-3.167725	-1.080526
1	0.347499	3.146600	1.004562
1	-0.347499	-3.146600	1.004562
1	-0.166290	3.167725	-1.080526
1	3.076840	-4.872630	-2.733627
1	2.023443	5.256654	4.275484
1	2.695539	3.615582	4.239561
1	0.990799	3.884363	3.834046

1	3.406595	4.880699	2.246759
1	1.059573	-5.575898	-3.976856
1	1.362418	-3.843926	-4.204322
1	0.076059	-4.384356	-3.116737
1	-3.406595	-4.880699	2.246759
1	-3.076840	4.872630	-2.733627
1	-6.115871	-2.637102	0.845435
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1	5.054361	-4.624033	-1.167096
1	5.889133	-3.080328	-0.856892
1	6.265138	-4.015979	-2.329164
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1	0.420533	5.255089	1.646929
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1	-1.718876	6.724899	-1.791284
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1	-6.265138	4.015979	-2.329164
1	-5.054361	4.624033	-1.167096
1	-0.076059	4.384356	-3.116737
1	-1.059573	5.575898	-3.976856
1	-1.362418	3.843926	-4.204322
1	-1.733904	-5.657672	0.528979
1	-1.588500	-6.499734	2.080905
1	-0.420533	-5.255089	1.646929
1	-0.990799	-3.884363	3.834046
1	-2.023443	-5.256654	4.275484

1	-2.695539	-3.615582	4.239561
1	-4.472349	0.713109	-1.230740
1	-4.509979	-0.452438	1.135441
1	4.509979	0.452438	1.135441
1	4.472349	-0.713109	-1.230740

DBC-H(56°)-2, optimized at the B3LYP/6-31G(d,p) level of theory.

	Cooedinates (Angstroms)		
Atomic Type	X	Y	Z
8	-4.649443	-2.83332	2.282223
8	4.419558	-3.189585	-2.357886
8	4.649443	2.83332	2.282223
8	-4.419558	3.189585	-2.357886
6	1.101155	-2.686549	-1.017934
6	2.494815	0.54801	0.306606
6	1.308451	2.590753	0.941499
6	1.295332	1.322446	0.32747
6	2.443432	-0.741083	-0.393689
6	1.186201	-1.421069	-0.407437
6	0.027633	0.695215	-0.039575
6	-0.027633	-0.695215	-0.039575
6	2.189129	-3.3014	-1.627663
6	3.525831	-1.292785	-1.129136
6	3.58604	2.29944	1.592442
6	2.443432	3.11896	1.543678
6	3.392297	-2.575908	-1.680006
6	-3.620383	-1.01214	1.040567
6	-2.443432	0.741083	-0.393689
6	3.620383	1.01214	1.040567
6	-3.58604	-2.29944	1.592442
6	-1.295332	-1.322446	0.32747
6	-2.494815	-0.54801	0.306606
6	-1.308451	-2.590753	0.941499
6	-3.392297	2.575908	-1.680006
6	-1.101155	2.686549	-1.017934

6	-1.186201	1.421069	-0.407437
6	2.050431	-4.660346	-2.303116
6	-3.525831	1.292785	-1.129136
6	-2.189129	3.3014	-1.627663
6	2.045379	4.277832	3.74491
6	2.430895	4.463116	2.263022
6	-2.443432	-3.11896	1.543678
6	1.041905	-4.61694	-3.466857
6	-2.430895	-4.463116	2.263022
6	-2.050431	4.660346	-2.303116
6	-5.842263	-2.077476	2.386711
6	5.656573	-2.512675	-2.481019
6	1.683105	-5.765254	-1.295294
6	5.842263	2.077476	2.386711
6	1.536292	5.513412	1.587436
6	-1.683105	5.765254	-1.295294
6	-5.656573	2.512675	-2.481019
6	-1.041905	4.61694	-3.466857
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1	0.380026	3.142838	1.005948
1	-0.380026	-3.142838	1.005948
1	-0.133517	3.169275	-1.07914
1	3.026277	-4.904194	-2.732241
1	2.077706	5.235443	4.27687
1	2.732791	3.587508	4.240947
1	1.030923	3.873907	3.835432
1	3.457386	4.843585	2.241255
1	1.001844	-5.586559	-3.97547
1	1.322587	-3.857812	-4.202936
1	0.030707	-4.384908	-3.115351
1	-3.457386	-4.843585	2.241255
1	-3.026277	4.904194	-2.732241
1	-5.682232	-1.137551	2.930773

1	-6.545238	-2.698109	2.944873
1	-6.266862	-1.84955	1.400135
1	6.105266	-2.302289	-1.501112
1	5.552111	-1.570039	-3.033971
1	6.312973	-3.183006	-3.038505
1	0.699842	-5.586641	-0.846658
1	2.412841	-5.822966	-0.48102
1	1.649227	-6.742318	-1.789898
1	6.545238	2.698109	2.944873
1	6.266862	1.84955	1.400135
1	5.682232	1.137551	2.930773
1	0.474866	5.250458	1.648315
1	1.79233	5.639435	0.530365
1	1.655643	6.482956	2.082291
1	-2.412841	5.822966	-0.48102
1	-1.649227	6.742318	-1.789898
1	-0.699842	5.586641	-0.846658
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1	-1.030923	-3.873907	3.835432
1	-2.077706	-5.235443	4.27687
1	-2.732791	-3.587508	4.240947
1	-4.455747	0.743438	-1.194487
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1	4.504968	0.392028	1.103239
1	4.455747	-0.743438	-1.194487