SUPPORTING INFORMATION

Double quantum ESR spectroscopy and quantum chemical calculations on a bis-BDPA molecule

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List of materials:

Materials and synthetic procedures for Compound 1, 3 and $3^{\cdot\cdot}$.

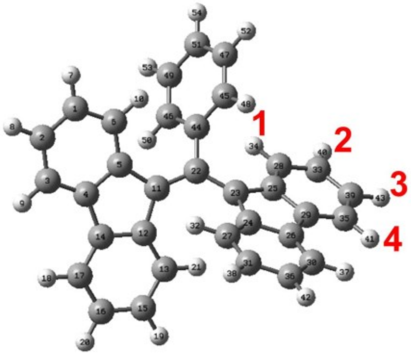
Materials. Synthesis were performed under argon atmosphere using standard Schlenck techniques. Chemicals, reagents and (dry) solvents were used as received from commercial vendors except diethylamine, which was dried over CaH_2 and destilled. Degassing of solvents and reagents were performed by severeal freeze-pump-thaw cycles. 2-Ethynylflourene [1] and 9-(Bromo-phenylmethylene)flourene (**2**)[2] were synthesized following literature procedures.

Compound 1: In a flame-dried round-bottom flask 0.75 g (1.85mmol) 4,4'-diiodobiphenyl and 0.027 g (0.038 mmol) $(Ph_3P)_2PdCl_2$ were dissolved in 30 mL of dry, degassed diethylamine.To this mixture 4 mg (0.019 mmol) CuI was added followed by a solution of 0.88 g (3.7 mmol) 2-ethynylflourene in 10 mL diethylamine. The mixture was stirred at room temperature for 17 h and finally warmed to 60 °C for an additional hour. After cooling to room temperature a very fine precipitate was obtained by filtration, which was recrystallized twice from toluene. Finally the solid was washed thoroughly with water and dried over $CaCl_2$ in a desiccator. Yield: 0.74 g (1.4 mmol), 76 %. Anal. Calcd. for $C_{42}H_{26}$ (530.67) C, 95.06; H, 4.94. Found: C, 89.75; H, 5.02. MS (MALDI): *m/z* (%) = 530.1 ($C_{42}H_{25}^+$, 100).

Compounds 3 and $3^{\cdot\cdot}$: A solution of 4.11 g (12.5 mmol) $K_3[Fe(CN)_6]$ in 25 mL deionized water was degassed for 1.5 h with a bubbling stream of argon. In a second round-bottom flask 207 mg (0.4 mmol) of compound **1**, 280 mg (0.8 mmol) 9-(Bromo-phenylmethylene)flourene (**2**) and 160 mg (1.7 mmol) NaO^tBu were suspended in dry, degassed DMF under argon. The initially green suspension turned deep blue after 2 min. of stirring. Stirring was continued for 1 hour at room temperature and then 1.7 mL (0.9 mmol) of the previously prepared $K_3[Fe(CN)_6]$ solution was added. After 30 min. a red-brown precipitate was filtered off, washed thoroughly with water and methanol and dried over KOH in a desiccator. From the 153 mg of the obtained solid 140 mg were recrystallized from 250 mL of a toluene/benzene mixture (4:1 v/v) at a bath temperature of 130 °C for 15 min. After cooling in an ice bath for 30 min a dark brown solid was obtained and dried over night in a desiccator. Yield: 33 mg (0.03 mmol), 8.5 %. MS (MALDI): *m/z* (%) = 338.81 (51), 525.52 (53), 527.51 (85), 529.30 ($[\mathbf{1}\text{-H}]^+$, 100), 531.56 (95), 717.20 (58), 719.17 (48), 1056.83 ($[M+Na]^+$, 14,), 1057.80 (15), 1058.79 (14), 1059.75 (13).

Table S1. Comparison between calculated geometrical parameters and crystal structure data (bond distances in Å , angles in °). Isotropic hyperfine couplings (HFC) are given in Gauss, hydrogen groups numbering (bold red) are given according to ref. 6.

	Exp.	Calcd.
	Ref. [3,4]	
C(11)-C(22)	1.405	1.415
C(22)-C(23)	1.413	1.415
C(22)-C(44)	1.495	1.495
C(23)-C(24)	1.467	1.470
C(24)-C(26)	1.405	1.422
C(26)-C(29)	1.464	1.464
C(11)-C(22)-C(23)	125.4	123.846
C(11)-C(22)-C(44)	116.6	118.076
C(23)-C(25)-C(24)	105.8	106.011
C(22)-C(23)-C(24)	127.6	126.791
	Ref. [4]	
C(11)-C(22)-C(23)-C(24)	31.7	34.359
C(11)-C(22)-C(23)-C(25)	151.5	150.040
	Ref. [5,6]	
HFC-(H-groups 1,3)	1.96	2.3
HFC-(H-groups 2,4)	0.67	0.6



Based on this optimized structure, HFCs were calculated (UB3LYP/6-31g*//UB3LYP/6-31g* (solvent: toluene)). There is a good agreement between the calculated value of 2.3 G for the larger proton hyperfine splitting, compared to the experimentally observed values (2.2 G or 1.96 G)[5,6]. The same holds for the smaller splitting, where the calculated values of 0.6-0.75 G are comparable with the experimental value of 0.67 G. Finally, the calculated isotropic g-factor of 2.0026(2) goes well along with the measured value of 2.0026[7]. Since this initial model could reasonably reproduce the experimental findings, we used it as a basis for the rest of calculations.

Table S2. HFC variation by rotation around θ(11,22,23,24) of BDPA radical calculated at UB3LYP/6-31g*

	model-0	model-10	model-20	model-30	model-40	model-50	model-60	model-70	model-80
H7	1.164	1.072	0.968	0.845	0.700	0.526	0.347	0.195	0.090
H8	-3.666	-3.352	-3.007	-2.607	-2.143	-1.597	-1.042	-0.578	-0.255
H9	0.862	0.791	0.722	0.644	0.551	0.434	0.302	0.182	0.094
H10	-3.710	-3.382	-3.018	-2.600	-2.122	-1.566	-1.007	-0.548	-0.234
H18	0.839	0.739	0.653	0.566	0.471	0.359	0.242	0.140	0.066
H19	1.144	1.032	0.923	0.807	0.673	0.512	0.344	0.198	0.091
H20	-3.632	-3.238	-2.852	-2.441	-1.983	-1.451	-0.916	-0.467	-0.149
H21	-3.616	-3.232	-2.852	-2.435	-1.949	-1.357	-0.718	-0.142	0.282
H32	-0.423	-1.008	-1.523	-2.022	-2.516	-3.021	-3.475	-3.809	-4.013
H34	-0.728	-1.233	-1.715	-2.195	-2.672	-3.139	-3.520	-3.775	-3.924
H37	0.195	0.305	0.399	0.489	0.577	0.676	0.780	0.876	0.959
H38	0.259	0.421	0.560	0.694	0.826	0.965	1.097	1.199	1.269
H40	0.259	0.424	0.576	0.723	0.864	0.997	1.101	1.170	1.211
H41	0.258	0.380	0.479	0.569	0.655	0.739	0.810	0.869	0.912
H42	-0.646	-1.136	-1.589	-2.048	-2.520	-3.022	-3.486	-3.829	-4.044
H43	-0.766	-1.274	-1.748	-2.216	-2.676	-3.121	-3.484	-3.734	-3.888
H48	0.151	0.240	0.285	0.317	0.327	0.297	0.214	0.123	0.044
H51	0.131	0.227	0.284	0.318	0.323	0.285	0.225	0.131	0.016
H52	-0.059	-0.081	-0.092	-0.094	-0.078	-0.035	-0.070	-0.045	0.143
H53	0.034	-0.017	-0.054	-0.082	-0.095	-0.090	0.028	0.090	-0.011
H54	0.096	0.228	0.302	0.349	0.360	0.314	0.214	0.083	-0.057
E(Hartree)	-1270.157502	-1270.160393	-1270.162384	-1270.163359	-1270.163292	-1270.162322	-1270.160863	-1270.159189	-1270.157621

Table S2. Continued

Table S1.Contd.

	model-90	model-100	model-110	model-120	model-140	model-150	model-160	model-170	model-180
H7	0.018	0.053	0.137	0.28411	0.606	0.750	0.871	0.998	1.119
H8	-0.027	-0.135	-0.393	-0.84164	-1.773	-2.247	-2.658	-3.101	-3.550
H9	0.034	0.066	0.139	0.2604	0.423	0.526	0.617	0.721	0.821
H10	-0.022	-0.117	-0.363	-0.80177	-1.730	-2.232	-2.647	-3.076	-3.605
H18	0.011	0.035	0.096	0.19544	0.512	0.606	0.676	0.741	0.847
H19	0.004	0.042	0.132	0.27674	0.634	0.784	0.902	1.010	1.137
H20	0.055	-0.058	-0.319	-0.74946	-1.929	-2.412	-2.804	-3.173	-3.592
H21	0.527	0.387	0.029	-0.53544	-1.900	-2.398	-2.810	-3.204	-3.543
H32	-4.049	-4.006	-3.889	-3.64271	-2.849	-2.405	-1.997	-1.543	-0.987
H34	-4.123	-4.079	-3.914	-3.58219	-2.690	-2.239	-1.806	-1.280	-0.560
H37	0.946	0.928	0.891	0.83023	0.685	0.607	0.531	0.435	0.298
H38	1.247	1.234	1.202	1.13222	0.911	0.786	0.670	0.535	0.358
H40	1.318	1.290	1.229	1.12896	0.881	0.752	0.622	0.463	0.260
H41	1.031	0.985	0.907	0.8064	0.613	0.527	0.446	0.349	0.217
H42	-4.035	-3.982	-3.855	-3.60627	-2.845	-2.419	-2.021	-1.569	-1.006
H43	-4.184	-4.127	-3.964	-3.65094	-2.742	-2.254	-1.795	-1.303	-0.734
H48	-0.115	-0.009	0.126	0.24825	0.336	0.325	0.292	0.247	0.133
H51	-0.043	0.005	0.088	0.20224	0.333	0.325	0.288	0.235	0.164
H52	0.058	0.006	-0.034	-0.06244	-0.096	-0.090	-0.069	-0.031	-0.052
H53	0.183	0.142	0.090	0.02508	-0.074	-0.090	-0.087	-0.077	0.031
H54	-0.196	-0.105	0.034	0.19677	0.369	0.360	0.305	0.220	0.074
E(Hartree)	-1270.155329	-1270.156716	-1270.158226	-1270.159910	-1270.162870	-1270.163457	-1270.162783	-1270.160740	-1270.157442

Table S3. Gross Mulliken spin populations of solvent optimized monomeric units with and without linker.

atom	0	0-linker	20	20-linker	30	30-linker	90	90-linker	150	150-linker	180	180-linker
C1	-0,06	-0,06	-0,05	-0,05	-0,05	-0,04	0,00	0,00	-0,04	-0,04	-0,06	-0,06
C2	0,15	0,15	0,11	0,11	0,10	0,10	0,00	0,00	0,09	0,09	0,14	0,14
C3	-0,05	-0,04	-0,03	-0,03	-0,03	-0,03	0,00	0,00	-0,03	-0,03	-0,04	-0,04
C4	0,11	0,11	0,08	0,08	0,08	0,08	0,00	0,00	0,07	0,06	0,10	0,10
C5	-0,13	-0,13	-0,10	-0,10	-0,10	-0,09	0,00	0,00	-0,08	-0,08	-0,12	-0,12
C6	0,15	0,15	0,12	0,12	0,11	0,11	0,00	0,00	0,10	0,09	0,15	0,14
C11	0,58	0,58	0,47	0,45	0,44	0,44	0,02	0,02	0,41	0,41	0,57	0,56
C12	-0,12	-0,12	-0,10	-0,10	-0,09	-0,09	0,00	0,00	-0,09	-0,09	-0,13	-0,12
C13	0,15	0,15	0,12	0,11	0,10	0,10	0,01	0,01	0,10	0,10	0,15	0,15
C14	0,11	0,11	0,08	0,07	0,07	0,07	0,00	0,00	0,07	0,07	0,11	0,11
C15	-0,06	-0,06	-0,05	-0,05	-0,04	-0,04	0,00	0,00	-0,04	-0,04	-0,06	-0,06
C16	0,15	0,15	0,11	0,11	0,10	0,10	0,00	0,00	0,10	0,10	0,15	0,14
C17	-0,05	-0,04	-0,04	-0,03	-0,03	-0,03	0,00	0,00	-0,03	-0,03	-0,05	-0,04
C22	-0,13	-0,13	-0,20	-0,20	-0,21	-0,20	-0,05	-0,05	-0,21	-0,21	-0,14	-0,14
C23	0,15	0,15	0,33	0,35	0,38	0,37	0,63	0,63	0,41	0,40	0,17	0,17
C24	-0,03	-0,03	-0,06	-0,07	-0,08	-0,07	-0,14	-0,14	-0,09	-0,08	-0,03	-0,03
C25	-0,03	-0,03	-0,07	-0,08	-0,08	-0,08	-0,14	-0,14	-0,08	-0,08	-0,03	-0,03
C26	0,02	0,02	0,05	0,05	0,06	0,06	0,12	0,12	0,07	0,07	0,03	0,03
C27	0,03	0,03	0,07	0,08	0,09	0,08	0,17	0,17	0,10	0,10	0,04	0,04
C28	0,03	0,03	0,08	0,08	0,09	0,09	0,17	0,17	0,10	0,09	0,03	0,03
C29	0,02	0,02	0,06	0,06	0,07	0,07	0,13	0,13	0,07	0,06	0,02	0,02
C30	-0,01	-0,01	-0,02	-0,02	-0,03	-0,02	-0,05	-0,05	-0,03	-0,03	-0,01	-0,01
C31	-0,01	-0,01	-0,03	-0,03	-0,04	-0,03	-0,07	-0,07	-0,04	-0,03	-0,02	-0,01
C33	-0,01	-0,01	-0,03	-0,04	-0,04	-0,04	-0,07	-0,06	-0,04	-0,04	-0,01	-0,01
C34	-0,01	-0,01	-0,02	-0,03	-0,03	-0,03	-0,05	-0,06	-0,03	-0,03	-0,01	-0,01
C36	0,03	0,03	0,07	0,07	0,08	0,07	0,16	0,17	0,10	0,09	0,04	0,04
C39	0,03	0,03	0,07	0,08	0,08	0,09	0,16	0,16	0,09	0,09	0,03	0,03
C43	0,02	0,02	0,03	0,03	0,04	0,03	0,01	0,01	0,04	0,04	0,02	0,02
C44	0,00	0,00	-0,01	-0,01	-0,01	-0,01	0,01	0,01	-0,01	-0,01	0,00	0,00
C45	0,00	0,00	-0,01	-0,01	-0,01	-0,01	0,01	0,01	-0,01	-0,01	0,00	0,00
C46	0,00	0,00	0,00	0,00	0,01	0,00	0,00	0,00	0,01	0,00	0,00	0,00
C48	0,00	0,00	0,00	0,00	0,01	0,00	0,00	0,00	0,01	0,00	0,00	0,00
C50	0,00	0,00	-0,01	-0,01	-0,01	-0,01	0,01	0,01	-0,01	-0,01	0,00	0,00

Table S3. Continued.

Linker atoms	0-linker	20-linker	30-linker	90-linker	150-linker	180-linker
C54	0,00	0,01	0,01	0,02	0,01	0,00
C55	0,00	-0,01	-0,01	-0,02	-0,01	-0,01
C56	0,00	0,01	0,00	0,01	0,00	0,00
C57	0,00	0,00	0,00	-0,01	0,00	0,00
C58	0,00	0,00	0,00	-0,01	0,00	0,00
C59	0,00	0,00	0,00	0,00	0,00	0,00
C61	0,00	0,00	0,00	0,00	0,00	0,00
C63	0,00	0,00	0,00	-0,01	0,00	0,00
C66	0,00	0,00	0,00	0,00	0,00	0,00
C67	0,00	0,00	0,00	0,00	0,00	0,00
C68	0,00	0,00	0,00	0,00	0,00	0,00
C69	0,00	0,00	0,00	0,00	0,00	0,00
C71	0,00	0,00	0,00	0,00	0,00	0,00
C73	0,00	0,00	0,00	0,00	0,00	0,00
C76	0,00	0,00	0,00	0,00	0,00	0,00
C77	0,00	0,00	0,00	0,00	0,00	0,00

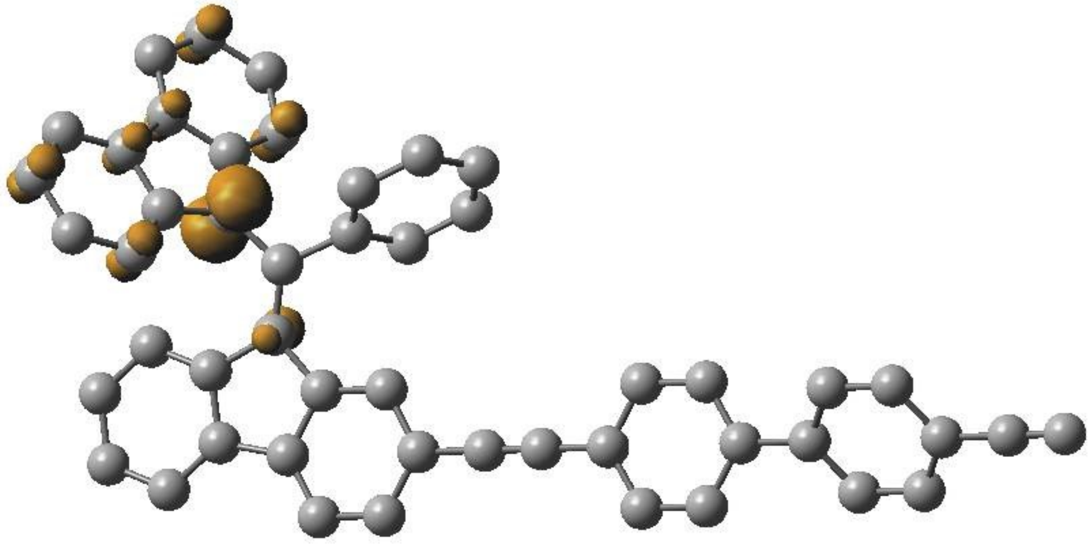


Fig. S1 Solvent optimized structure of linker attached to monomer (θ_1 =0.0) at position 2 of the fluorenyl ring. DFT-calculated SOMO spin density at 0.002 a.u. contour level.

Table S4. Calculated distances for trans conformations (in nm).

trans	0	30	90	150	180
0	2.55	2.44	2.20	2.24	2.23
30		2.08	n.a.	n.a.	n.a.
90			2.15	n.a.	n.a.
150				2.15	2.39
180					2.50

*n.a. = not available

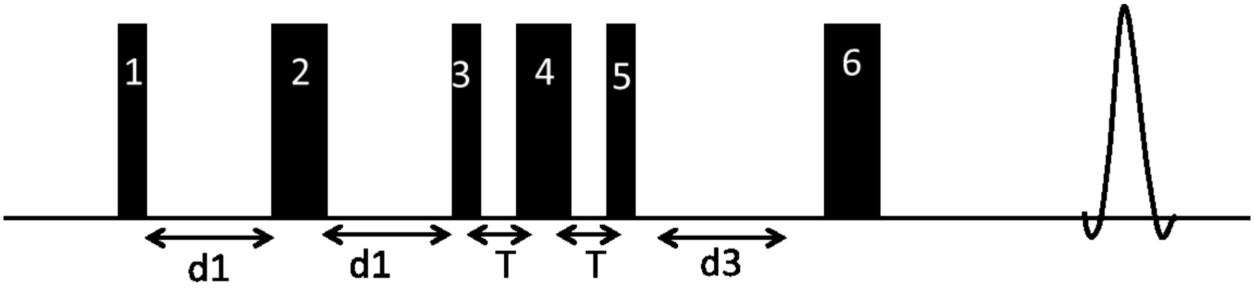
Table S5. Relative energies of optimized bis-BDPA radical model structures (in kcal/mol) at B3LYP/3-21G level.

		0	30	90	150	180
0	cis	7.88	4.09	n.a.	3.99	7.33
	trans	8.19	4.20	11.51	4.02	7.02
30	cis		0.17	7.47	0.1	n.a.
	trans		0.17	n.a.	n.a.	n.a.
90	cis			15.87	n.a.	n.a.
	trans			15.77	n.a.	n.a.
150	cis				0.00	3.43
	trans				4.82	3.50
						6.73
180	cis					7.02
	trans					

ΔE(20-20cis)=1.34kcal/mol

The 6-pulse DQC sequence used here is shown in Scheme S1. The actual initial pulse separations according to scheme 1 are as follow:

d1 : 460 ns
T : 104 ns
d2: 660 ns
d1 and d3 were incremented with 4 ns giving 8ns time steps in the dipolar evolution.
The averaging was done with 5 shots per point . 28 scans had been accumulated.



Scheme S1. 6-pulse DQC sequence

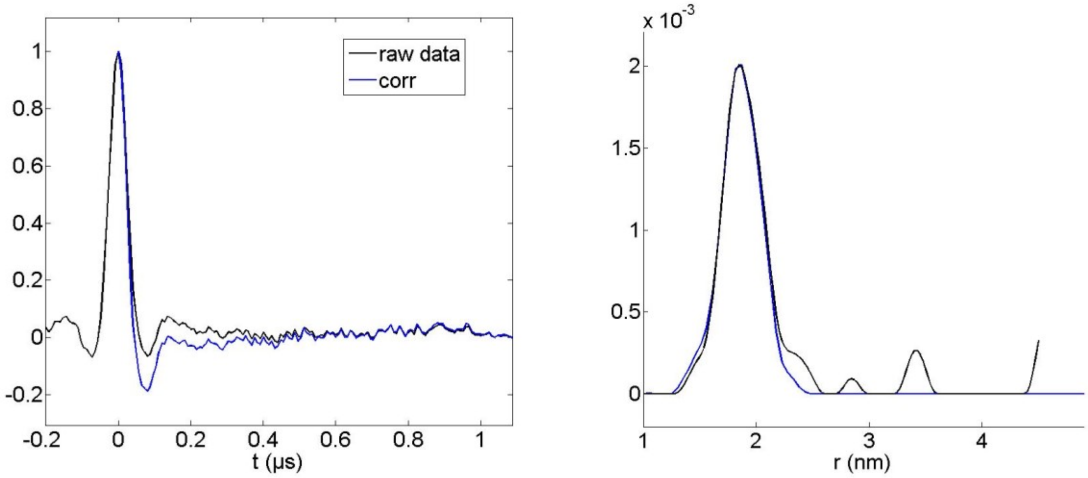


Fig S2. (left) DQC time domain data without (black) and with (blue) exponential background correction. (right) Distance distribution function obtained in both cases by Tikhonov regularization.

Table S6. Phase of cycle of 6-pulse DQC applied here.

P1	+x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y
P2	+x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y
P3	+x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y +x +y -x -y
P4	+x +x +x +x +y +y +y +y -x -x -x -x -y -y -y -y +x +x +x +x +y +y +y +y -x -x -x -x -y -y -y -y +x +x +x +x +y +y +y +y -x -x -x -x -y -y -y -y +x +x +x +x +y +y +y +y -x -x -x -x -y -y -y -y
P5	+x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x -x -x -x -x -x -x -x -x -x -x -x -x -x -x -x -x +y +y +y +y +y +y +y +y +y +y +y +y +y +y +y +y -y -y -y -y -y -y -y -y -y -y -y -y -y -y -y -y
P6	+x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x +x
inphase	+a -a +a -a +a -a +a -a +a -a +a -a +a -a +a -a -a +a -a +a -a +a -a +a -a +a -a +a -a +a -a +a +b -b +b -b +b -b +b -b +b -b +b -b +b -b +b -b -b +b -b +b -b +b -b +b -b +b -b +b -b +b -b +b
quadrature	+b -b +b -b +b -b +b -b +b -b +b -b +b -b +b -b -b +b -b +b -b +b -b +b -b +b -b +b -b +b -b +b -a +a -a +a -a +a -a +a -a +a -a +a -a +a -a +a +a -a +a -a +a -a +a -a +a -a +a -a +a -a +a -a

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