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The Influence of σ- and π-Acceptors on Two-Photon Absorption and Solvatochromism of Dipolar and Quadrupolar Unsaturated Organic Compounds**

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Quantum chemical calculation

The method B3LYP//6-31G*, which is integrated in Gaussian 98, was used for all ground state calculations. The geometry obtained after optimization of the ground state was taken for excited state calculations. Excited state parameters of the Franck-Condon states were calculated with ZINDO/S using a MRDCI scheme. Four reference determinants (ground state, HOMO→LUMO single excitation, HOMO→LUMO double excitation, HOMO-1→LUMO single excitation) were taken for excited state calculations.

Geometries of the Compounds Calculated

compound **6**


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\\#P RB3LYP/6-31G(D) POP=(FULL) TEST\\   a6-631-b3lyp\\0,1\C,0,6.111725
 ,-4.30246,0.916397\O,0,5.366638,-3.135651,0.614578\C,0,6.039108,-2.003
 723,0.241104\C,0,5.245834,-0.866272,-0.048569\C,0,8.053909,-0.749496,-
 0.246933\C,0,7.287796,0.386642,-0.537811\C,0,7.4339,-1.932175,0.13858\
 C,0,3.792053,-0.970642,0.067169\C,0,2.905273,0.022858,-0.176987\C,0,1.
 454315,-0.038528,-0.074036\C,0,0.697311,1.1118,-0.372894\C,0,-0.685776
 ,1.155319,-0.305176\C,0,-1.454239,0.038864,0.0726\C,0,-0.69725,-1.1114
 65,0.37149\C,0,0.685806,-1.154984,0.303726\C,0,-2.905197,-0.022537,0.1
 75507\C,0,-3.792023,0.970947,-0.068726\C,0,-5.245804,0.866531,0.046783
 \C,0,-6.039078,2.003845,-0.243484\C,0,-7.433884,1.932281,-0.141144\C,0
 ,-8.053909,0.74971,0.24472\C,0,-7.287781,-0.386276,0.536118\C,0,-5.900
 452,-0.319397,0.435593\F,0,1.28093,-2.322784,0.617264\F,0,-1.337097,-2
 .238907,0.745056\F,0,1.337143,2.239258,-0.746445\F,0,-1.280884,2.32309
 ,-0.61879\C,0,5.900467,0.319778,-0.437073\O,0,7.993347,1.500046,-0.907
 822\O,0,-5.366608,3.135651,-0.617386\O,0,-7.993378,-1.499588,0.906326\
 C,0,7.268921,2.679016,-1.213242\C,0,-6.111679,4.30246,-0.919174\C,0,-7
 .268875,-2.678177,1.213226\H,0,6.791229,-4.140854,1.7639\H,0,6.69162,-
 4.647781,0.050034\H,0,5.376938,-5.063889,1.184326\H,0,9.134415,-0.6876
 07,-0.328217\H,0,8.047485,-2.797791,0.358444\H,0,3.430023,-1.940781,0.
 376938\H,0,3.267593,0.997284,-0.488541\H,0,-3.267548,-0.996933,0.48698
 4\H,0,-3.429962,1.941116,-0.378464\H,0,-8.047485,2.79776,-0.361465\H,0
 ,-9.134415,0.68782,0.325882\H,0,-5.300827,-1.192642,0.658661\H,0,5.300
 842,1.193115,-0.65979\H,0,6.689606,3.034378,-0.350052\H,0,6.589447,2.5
 29007,-2.0634\H,0,8.015656,3.429962,-1.478394\H,0,-6.691544,4.647812,-
 0.052795\H,0,-6.791245,4.140869,-1.766663\H,0,-5.376877,5.063873,-1.18
 7134\H,0,-6.589661,-2.527161,2.0634\H,0,-6.6893,-3.034409,0.3506\H,0,-
 8.015625,-3.428894,1.478989\\Version=HP-PARisc-HPUX-G98RevA.9\HF=-1704
 .1729336\RMSD=1.274e-05\Dipole=0.0000125,0.0000671,0.0005845\PG=C01 [X
 (C26H22F4O4)]\\@
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compound **2**

\# RB3LYP/6-31G(D) OPT POP=(MINIMAL) TEST\\Untitled-2\\0,1\C,-8.0866256456,1.0429942051,0.1799780577\C,-7.3471295976,2.2443940083,0.0834474532\C,-5.9601821263,2.2253828178,0.0455617938\C,-5.2192762668,1.0296442444,0.0924495295\C,-5.9631230289,-0.1643846493,0.1772625838\C,-7.3477110071,-0.1661548603,0.2167741358\C,-3.763974586,1.0936688517,0.0448063605\C,-2.9098940702,0.042355291,0.0874188742\C,-1.4563147061,0.0727897346,0.0403803935\C,-0.6414053264,1.2152637078,-0.0660096469\C,0.7411454774,1.1401115442,-0.1043609294\C,1.4562928627,-0.0728160724,-0.0414822737\C,0.6413800894,-1.2153012205,0.064835809\C,-0.741160631,-1.1401467036,0.1032245992\C,2.9098651747,-0.0424274357,-0.0888499162\C,3.7639955324,-1.0936018536,-0.0438662967\C,5.2193012825,-1.0296039724,-0.0914140593\C,5.9631397686,0.164366159,-0.1771677731\C,7.3477259735,0.1661157835,-0.2166903595\C,8.0866259268,-1.0430222614,-0.179154193\C,7.3471525471,-2.2443438243,-0.0814845001\C,5.9602119333,-2.2252963261,-0.0434199744\N,9.4705190278,-1.0452573116,-0.2417137554\C,10.1948675936,-2.2861325468,-0.0267669857\C,10.1969586396,0.2102769096,-0.1532737019\N,-9.4705479315,1.0451844911,0.242523086\C,-10.1969753878,-0.2102248932,0.15202027\C,-10.1948333762,2.286184,0.0279829703\F,-1.4243276012,-2.2994278509,0.2064834563\F,1.1924192741,-2.4455509221,0.1347195652\F,-1.1924232943,2.4455165419,-0.1359439595\F,1.4242930873,2.2993933754,-0.207701241\H,-7.8549994908,3.2002042441,0.0359133504\H,-5.4273208469,3.1710710065,-0.0276848606\H,-5.4490012974,-1.1208724184,0.2082472557\H,-7.8618332224,-1.1181180764,0.2747412979\H,-3.3571669929,2.0963680392,-0.0313082486\H,-3.3160229412,-0.9611477061,0.1665708362\H,3.3159400183,0.9609208428,-0.1702106479\H,3.3572397375,-2.0961363561,0.0346514114\H,5.4490061493,1.1208280489,-0.2087128707\H,7.8618616612,1.1180341906,-0.2752812314\H,7.8550370795,-3.2001119136,-0.0332597261\H,5.4273539527,-3.1709237519,0.0306317001\H,11.2646944138,-2.0996079119,-0.1371017977\H,9.9119793016,-3.041395986,-0.7701309606\H,10.0205269486,-2.7124080524,0.9738630817\H,11.266892338,0.0104684428,-0.2362272196\H,10.0177978315,0.7388670365,0.7962153354\H,9.9219530748,0.8846654032,-0.9734379084\H,-11.2669020671,-0.0105611754,0.2354515853\H,-9.9219197875,-0.8859376944,0.9710648367\H,-10.0178691074,-0.7372426956,-0.7983504306\H,-11.2646489786,2.0997188437,0.1385591754\H,-10.0206879811,2.7126974518,-0.9725863439\H,-9.911702934,3.0412058066,0.7714833529\\Version=SGI64-G98RevA.7\HF=-1514.0266355\RMSD=6.971e-09\RMSF=4.463e-06\Dipole=0.0006076,0.0000104,-0.0000822\PG=C01 [X(C26H24F4N2)]\\@

compound **7**

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\# RB3LYP/6-31G(D) OPT POP=(MINIMAL) TEST\\Untitled-3\\0,1\C,-9.976513
7078,-0.967856649,-3.3701143021\C,-9.4873397767,-2.1817925529,-2.83405
12445\C,-8.1944917808,-2.2720988044,-2.3392491354\C,-7.3094154945,-1.1
769295657,-2.3339231211\C,-7.8075109769,0.0328564287,-2.859519025\C,-9
.0949976042,0.142214443,-3.3584055629\C,-5.9682160738,-1.3401148524,-1
.7969623736\C,-4.9812474037,-0.4113501027,-1.7080910896\C,-3.685967128
5,-0.6928002449,-1.1513641267\C,-2.6968258408,0.2362764803,-1.06026082
72\C,-1.3595257583,0.0729010906,-0.5212480144\C,-0.8170712051,-1.10685
07719,0.0241104097\C,0.4746437398,-1.1711993271,0.5178685368\C,1.35956
35473,-0.0731181532,0.5211783495\C,0.8171098746,1.1066337871,-0.024178
4085\C,-0.4746052711,1.1709825468,-0.5179370093\C,2.6968641593,-0.2364
848347,1.0601970518\C,3.6860069524,0.6925928777,1.1512505975\C,4.98129
69774,0.4111858675,1.7079792723\C,5.9682448632,1.3399795965,1.79677992
66\C,7.3094601254,1.1768641345,2.3337199495\C,7.8079543421,-0.03315092
52,2.8584138004\C,9.0953928624,-0.1423912237,3.3574477599\C,9.97645562
6,0.9680289027,3.3702277518\C,9.4869183242,2.1821761076,2.8349736588\C
,8.1941309457,2.2723534565,2.3399867003\N,11.2564965203,0.8679026406,3
.8899947551\C,12.1855159912,1.9728804343,3.725729042\C,11.7822332268,-
0.4346022013,4.2626744964\F,-0.8932281109,2.3514725578,-1.0179671646\F
,1.5569077871,2.233635585,-0.0828096001\F,0.893266581,-2.3516894778,1.
0179015977\F,-1.5568713954,-2.2338514214,0.0827449548\N,-11.2566303125
,-0.86761864,-3.8896661163\C,-11.7819097497,0.4347965318,-4.2633012471
\C,-12.1860503565,-1.9721061239,-3.7243469195\H,-10.1187702232,-3.0614
859288,-2.8010821837\H,-7.8551719092,-3.2242907903,-1.9366871698\H,-7.
1740891062,0.915369446,-2.8752166437\H,-9.4211715987,1.1016123091,-3.7
419123595\H,-5.7432963424,-2.3400980299,-1.4230442678\H,-5.1503046832,
0.603421536,-2.0671801646\H,-3.5183954426,-1.7036464101,-0.7942542377\
H,-2.9071806759,1.2363726391,-1.4301029386\H,2.9072125038,-1.236568299
4,1.4300767858\H,3.5184344945,1.7034199677,0.7940860516\H,5.1503596248
,-0.6035432628,2.0671850485\H,5.7432595705,2.339961536,1.42289751\H,7.
1749275489,-0.9159641743,2.873152938\H,9.4218924769,-1.1019711826,3.74
02219127\H,10.1180100257,3.0621398349,2.8027884138\H,7.8545271578,3.22
47141131,1.9380628415\H,13.1282524269,1.7233124066,4.2161669362\H,11.7
996010517,2.8860152602,4.1952283564\H,12.3959199975,2.1973577669,2.668
1025504\H,12.7877771949,-0.3108551247,4.6689775204\H,11.8381195807,-1.
1301524296,3.4105263497\H,11.1662126097,-0.9012275451,5.0409876005\H,-
12.7876123966,0.3111363083,-4.6692368881\H,-11.1658933573,0.9005117031
,-5.0421644899\H,-11.837279573,1.1310850346,-3.4117233494\H,-13.128816
0494,-1.7225206735,-4.214718585\H,-12.3962593456,-2.1957164385,-2.6664
995788\H,-11.8006233474,-2.8857408839,-4.1932758975\\Version=SGI64-G98
RevA.7\HF=-1668.8418551\RMSD=8.829e-09\RMSF=1.699e-06\Dipole=-0.000035
5,0.0002038,0.0000846\PG=C01 [X(C30H28F4N2)]\\@
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compound **8**

\# RB3LYP/6-31G(D) OPT POP=(MINIMAL) TEST\\Untitled-1\\0,1\C,-0.3130966312,-0.3348049337,0.5827900683\C,0.1094987084,0.2781720607,-0.5482685497\C,0.5299013027,-0.9085051757,1.6242258806\C,-0.7066517957,0.8628544894,-1.6064791906\C,1.9389996614,-0.8942755678,1.6076038253\C,2.6907691872,-1.4534313185,2.6272984376\C,2.0720544551,-2.0759555251,3.7411493067\C,0.6578159789,-2.0851580211,3.7688570242\C,-0.0772187997,-1.5197425245,2.7371158814\N,2.8202277318,-2.6517162609,4.7517029953\C,-0.0612371546,1.4534720508,-2.7117072926\C,-0.7428068828,2.0384066941,-3.7715622526\C,-2.1348297269,2.0565164218,-3.7682693545\C,-2.8177062584,1.4853236056,-2.6975980461\C,-2.1131572865,0.9057403389,-1.6480716865\F,1.2841728939,1.4632545007,-2.7647645019\F,-0.0685403281,2.5827145257,-4.7924751856\F,-2.8090209602,2.614604409,-4.7791976607\F,-4.1568070315,1.4961701823,-2.6818718131\F,-2.8471332216,0.3758193841,-0.6507559094\C,2.1559548845,-3.1525167909,5.942922304\C,4.2643143801,-2.4889517512,4.7655470706\H,-1.3786439448,-0.4264561101,0.7639943073\H,1.1754786898,0.3673454383,-0.7307792153\H,2.4661198126,-0.430254948,0.7787402058\H,3.7710336861,-1.4051118441,2.560040601\H,0.1274731093,-2.5342357416,4.599943297\H,-1.1632925049,-1.5477867915,2.7943078536\H,2.9005646499,-3.586070199,6.6127106976\H,1.4349049156,-3.9406978635,5.6925860273\H,1.6191211497,-2.3624426178,6.4905319799\H,4.6757943574,-3.0206545665,5.6252483058\H,4.5694199793,-1.4335244537,4.836174348\H,4.72076567,-2.9140278106,3.862845703\\Version=HP-PARisc-HPUX-G98RevA.9\HF=-1170.8121291\RMSD=2.939e-09\RMSF=1.367e-06\Dipole=1.1277632,-0.961127,1.9148803\PG=C01 [X(C16H12F5N1)]\\@

compound **9**

\# RB3LYP/6-31G(D) OPT POP=(MINIMAL) TEST\\Untitled-1\\0,1\C,1.8823331426,-0.4399666046,0.3470729399\C,2.8163958477,-1.2261140202,1.1359024277\C,0.5277166109,-0.4080217374,0.4341849361\C,2.4306988194,-2.1221874966,2.1538955141\C,3.3573349068,-2.8528032183,2.8785816958\C,4.7481689596,-2.7276383173,2.632225754\C,5.1415688125,-1.8378839477,1.6050569782\C,4.1984708352,-1.1144391169,0.8904435428\N,5.6774957933,-3.4406708335,3.3682289938\C,-0.2904502807,0.4186595273,-0.4124976118\C,-1.6460363723,0.4556995372,-0.3331933413\C,-2.5727759431,1.2459406342,-1.1312659462\C,-3.9561344303,1.1331808858,-0.8835614179\C,-4.9172002711,1.8442152538,-1.5910151244\C,-4.5231191339,2.718791098,-2.600160359\C,-3.1670022543,2.8641483432,-2.8816962673\C,-2.2233400452,2.1417856234,-2.1601483168\F,-4.3899275262,0.3014158477,0.0812709052\F,-6.2171893605,1.6930019041,-1.3079752752\F,-5.4346772898,3.411033466,-3.290992052\F,-2.7754285605,3.7022911763,-3.8499663998\F,-0.932443038,2.3360098019,-2.4905262895\C,5.2308829279,-4.4592004669,4.3037959773\C,7.0789076549,-3.4047916891,2.9859236113\H,2.3454108491,0.2000198106,-0.4055712478\H,0.0096846268,-1.0249036878,1.1676733578\H,1.3774175982,-2.256365362,2.3839198748\H,2.9981962377,-3.5304627649,3.6438395292\H,6.1892268757,-1.7099429121,1.3609399761\H,4.541107424,-0.4392506274,0.109073707\H,0.2308529169,1.03119105,-1.1407936324\H,-2.1275956805,-0.1735879451,0.410225973\H,6.1000959718,-4.8940297138,4.8003686894\H,4.6742070649,-5.2713924708,3.811066212\H,4.5862788705,-4.0288692616,5.0802154276\H,7.6574244716,-4.0051330632,3.6902774287\H,7.4726357491,-2.3813392218,3.0204146429\H,7.2510597272,-3.8012534869,1.9731791526\\Version=HP-PARisc-HPUX-G98RevA.9\HF=-1248.2195537\RMSD=7.419e-09\RMSF=2.210e-06\Dipole=2.063911 4,-1.3590779,1.1984464\PG=C01 [X(C18H14F5N1)]\\@

compound **10**

\# RB3LYP/6-31G(D) OPT POP=(MINIMAL) TEST\\Untitled-1\\0,1\C,3.5393425875,-3.3134994897,3.0828153938\C,4.73786017,-3.6048537599,3.7168734986\C,3.3179879028,-2.0977080154,2.4069821208\C,5.8035605353,-2.6744144115,3.7179603224\C,4.3884478376,-1.1795285047,2.4029683369\C,2.0387245787,-1.8581045349,1.7616033412\C,1.6409374831,-0.7592533194,1.0675773721\C,5.5920892806,-1.45205853,3.0309642715\N,6.9972952215,-2.940751912,4.3645448961\C,7.2347139885,-4.2609842209,4.9230942298\C,0.3432513434,-0.6323555185,0.4681229949\C,-0.0902218326,0.4502284746,-0.2354559537\C,8.1203955921,-2.0312292794,4.211901555\C,-1.3969262947,0.5441508361,-0.8233441514\C,-1.8215690277,1.6279837447,-1.5257325038\C,-3.112770533,1.8376774058,-2.1636865643\C,-4.1908819484,0.9313627622,-2.1681222857\C,-5.3988547312,1.2016191798,-2.800989096\F,-4.0887646381,-0.2575929226,-1.5449849695\C,-5.5832223695,2.4103688992,-3.4677379242\F,-6.3890942524,0.3006304911,-2.7715184235\F,-6.7425096226,2.6757845882,-4.0781427305\C,-4.5454998776,3.3384732096,-3.4906485856\C,-3.3475379918,3.0463148232,-2.8511808164\F,-4.7069840516,4.5050874876,-4.1274196471\F,-2.3773573456,3.977110641,-2.9034232933\H,2.7431374621,-4.0547021399,3.1059816863\H,4.8446556434,-4.5621627107,4.2125856686\H,4.2803978037,-0.2270342185,1.89171117\H,1.3189554338,-2.6727364636,1.8559243288\H,2.3199150767,0.0836044409,0.9431343443\H,6.3787693469,-0.7083591029,2.9866626366\H,8.2115357021,-4.2731512421,5.4098944784\H,7.221646057,-5.0524843564,4.1576659301\H,6.4825996133,-4.5110262658,5.6817087239\H,-0.3388216988,-1.4750903318,0.5926427812\H,0.5822943834,1.2987169068,-0.3671110108\H,8.9580256883,-2.3943775174,4.8099670531\H,7.8677271971,-1.0259710689,4.5711638611\H,8.4560051206,-1.9446899463,3.1667877424\H,-2.054252843,-0.3077053305,-0.6829384095\H,-1.1302275026,2.4581116578,-1.6419870181\\Version=HP-PARisc-HPUX-G98RevA.9\HF=-1325.6269876\RMSD=6.627e-09\RMSF=2.606e-06\Dipole=2.4881891,-1.0101083,1.4206058\PG=C01 [X(C20H16F5N1)]\\@

Materials

Compounds **1** und **6** were synthesized according to published procedures[1,2].

Part 1

General Information. All manipulations were performed under an inert argon atmosphere using standard techniques. Reagents and solvents were purchased from Aldrich and used without further purification. Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analysis was carried out at the University of Massachusetts Microanalytical Laboratory. NMR spectra were obtained using a Bruker DPX300 NMR spectrometer. Mass spectra were taken with a SSQ 710 (Finnigan) at the University of Potsdam.

Pentafluorobenzyltriphenylphosphonium bromide (**P1**). A mixture of pentafluorobenzyl bromide (5.40 g, 20.69 mmole) and of triphenylphosphine (5.43 g, 20.70 mmol) was heated under nitrogen in anhydrous toluene (30 mL) at 80^0C for 4 hrs. The white precipitate obtained was filtered while hot followed by washing with toluene. The material obtained was suspended in diethyl ether (150 mL), stirred for 1 h and filtered. After drying under vacuum a white powder was obtained with 92% yield. ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.85 (m, 9H), 7.72 (m, 6H), 5.59 (d, *J* = 13.4 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25°C, TMS): 136.1, 136.14, 134.4, 134.3, 131.0, 130.8, 117.6, 116.4, 21.6; elemental analysis calcd (%) for $C_{25}H_{17}BrF_5P$ (523.3): C 57.39, H 3.25, Br 15.27, F 18.16; found: C 57.13, H 3.27, Br 15.41, F 17.98.

E-**Dimethyl-[4-(2-pentafluorophenyl-vinyl)-phenyl]-amine** (**8**). Sodium (0.23 g) was slowly put in anhydrous ethyl alcohol (15 mL). The solution obtained was added under nitrogen to a mixture of the phosphonium salt **P1** (5.25 g, 10.04 mmol) and 4-dimethylamino-benzaldehyde (1.50 g, 10.04 mmol). The latter was dissolved in a chloroform-ethanol mixture (50 mL; 20 mL chloroform, 30 mL ethanol). The solution obtained was stirred at room temperature overnight. The reaction mixture was quenched with 2% hydrochloric acid (3 mL) and extracted with chloroform (3x100 mL). The combined organic layer was washed with water and brine, and dried over magnesium sulfate. After removal of solvent, the solid was recrystallized from ethanol yielding product **8** as a *trans*-*cis* (40:60) mixture. ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 7.42 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 16.6 Hz, 1H-*trans*), 7.08 (d, *J* = 8.40 Hz, 1H-*cis*), 6.75 (d, *J* = 16.6 Hz, 1H-*trans*), 6.70 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 1H-*cis*), 3.01 (s, 6H for *trans*), 2.90 (s, 6H for *cis*); elemental analysis calcd (%) for $C_{16}H_{12}F_5N$ (313.1): C 61.34, H 3.86, F 30.32; found: C 61.19, H 3.82, F 30.23.

The *trans*-*cis* mixture of **8** (1.05 g, 3.35 mmol) was heated under nitrogen in toluene (40 mL) at reflux with a catalytic amount of iodine (10 mg) for 24 hrs. The solvent was evaporated. The product obtained was recrystallized from ethanol resulting in yellowish-green crystals of **8** (35%

yield). m.p. 172-173^{0}C; ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 7.42 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 16.6 Hz, 1H), 6.75 (*d*, *J* = 16.6 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 2H), 3.01 (*s*, 6H). MS(70 eV): *m/z* (%): 313 (100) [$M^{+\bullet}$], 219 (8), 156 (7), 83 (5); elemental analysis calcd (%) for $C_{16}H_{12}F_5N$(313.3): C 61.34, H 3.86, F 30.32; found: C, 61.26; H, 3.88; F, 30.26.

Dimethyl-[4-(4-pentafluorophenyl-buta-1*E*,3*E*-dienyl)-phenyl]-amine (**9**).

The general procedure described for the manufacture of **8** was applied for synthesis of **9**. The starting materials used were **P1** and 4-3-(4-dimethylamino-phenyl)-propenal (dimethylaminocinnamaldehyde). Both compounds were dissolved (same molar concentrations as for the manufacture of **8**) in THF (50 mL) under nitrogen at room temperature. Furthermore, the isomerization with iodine was similarly performed as decribed for **8**. Yellow crystals of **9** were obtained after recrystallization from chloroform (53% yield). m.p. 187-188 °C; ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 7.37 (d, *J* = 8.6 Hz, 2H), 7.26 (m, 2H), 6.82 (m, 3H), 6.43 (d, *J* = 16 Hz, 1H), 3.0 (s, 6H). MS(70 eV): *m/z* (%): 339 (65) [$M^{+\bullet}$], 172 (100) [$M^{+\bullet}$-$C_6F_5^+$], 158 (25), 157 (29), 127 (29); elemental analysis calcd (%) for $C_{18}H_{14}NF_5$ (339.3): C 63.72, H 4.16, F 28.00; found: C 63.58, H 4.11, F 28.13.

Dimethyl-[4-(6-pentafluorophenyl-hexa-1*E*,3*E*,5*E*-trienyl)-phenyl]-amine (**10**). The general procedure described for the manufacture of **8** was applied for synthesis of **10**. The starting materials **P1** and 5-[4-(dimethylamino)phenyl]-2,4-pentadienal were dissolved in THF (50 mL) under nitrogen at room temperature. Isomerization with iodine was similarly performed as described for **8**. Red crystals were obtained after recrystallization from chloroform (47% yield). m.p. 196°C; ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 7.33 (d, *J* = 9.0 Hz, 2H), 7.19 (d, *J* = 16.0 Hz, 1H), 7.15 (d, *J* = 16.0 Hz, 1H), 6.65 (m, 5H), 6.39 (d, *J* = 16.6 Hz, 1H), 2.99 (s, 6H); MS(70 eV): *m/z* (%): 365 (100) [$M^{+\bullet}$], 183 (16) [$C_7H_2F_5^+$], 172 (18) [$C_{12}H_{14}N^+$], 134 (42) [$C_9H_{12}N^+$]; elemental analysis calcd (%) for $C_{20}H_{16}NF_5$ (365.3): C 65.75, H 4.41, F 26.00; found: C 65.60, H 4.40 F 26.12.

***(E,E)*-1,4-Bis[4-(*N*,*N*-di-*n*-butylamino)phenylethenyl]-2,3,5,6-tetrafluorobenzene** (**2**).

[4-(Dimethoxy-phosphorylmethyl)-2,3,5,6-tetrafluoro-benzyl]-phosphonic acid dimethyl ester[1] (0.43 g, 1.09 mmol) was dissolved in THF (5 mL) and added to a suspension of sodium hydride (0.35 g) in THF (5 mL) under nitrogen. The mixture obtained was stirred at room temperature at room temperature for 10 min. A solution of 4-*N*, *N*-di-*n*-butylaminobenzaldehyde (0.51 g, 2.18 mmol) in THF (5 mL) was added to this suspension and stirred at room temperature for 20 hrs. The reaction mixture was poured into ice-water. The red precipitate was filtered, dried and recrystallized from chloroform to give red crystals (56% yield). The isomerization was performed as described for compound **8**. m.p. 141-143°C; ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 7.38

(*d*, *J* = 9.0 Hz, 4H), 7.36 (*d*, *J* = 16.60 Hz, 2H), 6.82 (*d*, *J* = 16.80 Hz, 2H), 6.61 (*d*, *J* = 9.0 Hz, 4H), 3.28 (*t*, *J* = 7.60 Hz, 8H), 1.57 (*m*, 8H), 1.35 (*m*, 8H), 0.96 (*t*, *J* = 7.60 Hz, 12H). ^{13}C-NMR (75 MHz, $CDCl_3$, 25°C, TMS): 148.9, 143.4,136.8, 128.7,124.4, 114.9, 111.9, 109.2, 51.1, 29.8, 20.7, 14.4; MS(70 eV): *m/z* (%): 608 (100) [$M^{+\bullet}$], 565 (42) [$C_{35}H_{41}F_4N_2^+$], 523(17) [$C_{32}H_{35}F_4N_2^+$], 423 (11) [$C_{25}H_{19}F_4N_2$], 83 (79); elemental analysis calcd (%) for $C_{38}H_{48}F_4N_2$ (608.8): C 74.97, H 7.95, F 12.48; found: C 75.18, H 7.82, F 12.26.

(E,E,E,E)-**1,4-Bis[4-[4'-(*N,N*-dimethylamino)phenyl]-1,3-butadienyl]-2,3,5,6-tetrafluorobenzene 7**. The general procedure described for the manufacture of **2** was applied for synthesis of **7**. The aldehyde used was 4-3-(4-dimethylamino-phenyl)-propenal. m.p. 196-197°C; MS(70 eV): *m/z* (%): 492 (100) [$M^{+\bullet}$], 246 (48) [$C_{15}H_{14}F_2N^+$], 172 (66) [$C_{12}H_{14}N^+$]; elemental analysis calcd (%) for $C_{30}H_{28}F_4N_2$ (492.6): C 73.15, H 5.73, F 15.43; Found: C 73.34, H 5.58, F 15.29.

Part 2

IR–Spectra (in KBr) were taken with a Beckman Acculab 4. NMR–Spectra were measured in $CDCl_3$ using a Bruker AC 200 and AM 400 at room temperature. Mass spectra were taken with a MAT 95 spectrometer (FD). Combustion analyses were performed in the microanalytical laboratory of the Chemical Institute at the Johannes Gutenberg–Universität, Mainz, Germany. Melting points were not corrected. The eluent mixtures are given in v/v. Chemicals were used as received. Solvents were dried according to standard procedures and distilled. Diethyl 2,5-dicyano-4-[(diethoxyphosphoryl)methyl]benzylphosphonate was prepared from 2,5-dimethylterephthalodinitrile according to literature procedures[3,4].

2,5-Bis(bromomethyl)benzonitrile

A mixture of 2,5-dimethylbenzonitrile (7 g, 0,05 mol), NBS (17,8 g 0,1 mol) and AIBN (50 mg) in CCl_4 (50 ml) was heated to reflux for 6 h. Succinic imide was separated by filtration, washed with CCl_4 (15 ml). The solvent was evaporated. Purification was performed by chromatography on silica gel using petroleum ether with increasing content of ethyl acetate as eluent. yield: 4,6 g (32%); colorless powder, mp. 88°C; IR (KBr): 3000, 2920, 2850, 2225, 1485, 1435, 1410, 1222, 1210, 1199, 903, 852, 660 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 4.43/4.65 (2 x *s*, 4H, CH_2Br); 7.51 (d, *J* = 8.1 Hz, 1H, 3-H); 7.58 (d, 1H, 4-H); 7.66 (s, 1H, 6-H); ^{13}C-NMR ($CDCl_3$) 28.7, 30.6 (CH_2Br); 116.1 (CN); 130.9, 133.3, 33.7 (CH); 112.7, 139.0, 140.8 (C-1, C-2, C-5); MS(70 eV): *m/z* (%): 289 (5) [$M^{+\bullet}$], Br_2-pattern; 208 (75) [$M^{+\bullet}$-HBr]; 130 (100) [$M^{+\bullet}$-Br_2]); elemental analysis calcd (%) for $C_9H_7Br_2N$ (289.0): C 37.41, H 2.44, N 4.85, Br 55.30; found: C 37.80, H 2.32, N 4.66, Br 54.60.

Diethyl 2-cyano-4-[(diethoxyphosphoryl)methyl]benzylphosphonate

yield: 79%; yellowish oil; IR (neat): 2970, 2900, 2222, 1488, 1245, 1160, 1020, 955, 815;

^{1}H-NMR ($CDCl_3$): 1.20 (m, 12 H, CH_3), 3.06 (d, *J* = 22 Hz, 2 H, CH_2-P), 3.28 (d, *J* = 22 Hz, 2 H, CH_2-P), 4.00 (m, 8 H, OCH_2) 7.41 (s, 2 H, 5-H, 6-H) 7.50 (*s*, 1 H, 3-H), ^{13}C-NMR ($CDCl_3$): 16.2 (m, CH_3), 31.9 (d, *J* = 137 Hz, CH_2-P), 33.0 (d, *J* = 138 Hz, CH_2-P), 62.4 (m, OCH_2), 113.5 (d, *J* = 4.9 Hz, C-2) 117.4 (CN) 131.2 (bs, CH) 131.8 (m, 2 C_q, C-1, C-4) 133.7 (dd, *J* = 3 Hz, *J´*= 7 Hz, CH) 134.1 (dd, *J* = 3 Hz, *J´*= 7 Hz, CH); elemental analysis calcd (%) for $C_{17}H_{27}NO_6P_2$ (403.3): C 50.62, H 6.75, N 3.47; found: C 50.30, H 6.51, N 3.19.

Diethyl 4-[(diethoxyphosphoryl)methyl]-2-[(2-ethylhexyl)sulfanyl]-5-(propylsulfanyl)benzylphosphonate

Hydrogen bromide in acetic acid (0.08 mol, 33%, 20 g) was added to a solution of 1-(2-ethylhexylsulfanyl)-4-propylsulfanylbenzene (0.02 mol, 6g) in glacial acetic acid (10 mL). Paraformaldehyde (0.06 mol, 1.8 g) was added to the stirred solution. The mixture was slowly heated, refluxed for 8 h and finally poured on ice (100 g). The solution obtained was neutralized with Na_2CO_3 and extracted with toluene (3 x 30 ml). The combined organic solutions were washed with aq. $NaHCO_3$, brine and dried over $MgSO_4$. After evaporation of the solvent, ^{1}H-NMR showed a mixture of the bis-bromomethyl thioether and the isomeric mono-bromomethyl compounds. This mixture was added to triethyl phosphite (8.8 g, 0.05 mol) and heated to 170°C for 3.5 h. Unchanged reagent was distilled. The residue was purified by chromatography on silica gel using toluene/ethyl acetate (3/1) to elute the mono-phosphonate followed by ethyl acetate to isolate the pure bisphosphonate. yield: 6.2 g (52%); yellowish oil; IR (neat): 2950, 2905, 2850, 1460, 1435, 1385, 1360, 1240, 1163, 1040, 970, 900, 850, 825 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 7.40 (d, *J* = 2 Hz, 1 H), 7.38 (d, *J* = 2 Hz, 1 H, 3-H, 6-H), 4.02 (m, 8 H, OCH_2) 3.40 (d, *J* = 21.6 Hz, 4 H, CH_2P) 2.84 (m, 4 H, SCH_2) 1.63 (m, 3 H) 1.45 – 1.26 (m, 6 H), 1.22 (m, 14 H, CH, CH_2, CH_3), 0.96 (t, 3 H, CH_3) 0.83 (m, 6 H, CH_3); ^{13}C-NMR: 10.7, 13.4, 13.5 CH_3; 16.3 (d, *J* = 5.8 Hz, CH_3 eth), 22.4 (CH, CH_2), 22.9 (CH, CH_2), 25.7 (CH, CH_2), 28.7 (CH, CH_2), 32.5 (CH, CH_2), 36.9 (CH, CH_2), 39.0 (CH, CH_2), 39.5 (CH, CH_2), 30.7 (d, *J* = 136 Hz, CH_2P), 30.8 (d, *J* = 136 Hz, CH_2P) 62.1 (d, *J* = 5.8 Hz, OCH_2), 131.2 (d, *J* = 5.5 Hz, C-CH_2-P) 131.6 (d, *J* = 5,.5 Hz, C-CH_2-P), 132.1 (d, *J* = 2.4 Hz, CH), 132.4 (d, *J* = 2.4 Hz, CH), 134.3 (d, *J* = 3.7 Hz, C-S) 135.6 (d, *J* = 3.7 Hz, C-S); MS (FD) *m/z* (%): 576.2 (100) [$M^{+\bullet}$], 278 (7) [M^{2+}]; elemental analysis calcd (%) for $C_{27}H_{50}O_6P_2S_2$ (596.8): C 54.34, H 8.45, S 10.75; found: C 54.67, H 8.67, S 10.43.

diethyl 4-[(diethoxyphosphoryl)methyl]-2-[(2-ethylhexyl)sulfonyl]-5-(propylsulfonyl)benzylphosphonate

The bis-thioether (4.8g, 0.008 mol) was dissolved in dichloromethane (40 mL) and *m*-chloroperoxybenzoic acid (0.048 mol, 12.9 g of 65% *m*-CPBA) was added in several protions, so that the temperature of the stirred solution was kept between 30 and 25°C. After 1 h stirring, the

mixture was filtered, the residue washed with CH_2Cl_2 (20 mL) and the combined organic solutions washed with 2M NaOH (2 x 15 mL), and brine (10 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue purified by chromatography on silica gel (5 x 12 cm) with ethyl acetate as an eluent. yield: 4.9 g (92%); colorless oil; IR (neat): 2950, 2905, 2845, 1460, 1443, 1430, 1375, 1355, 1290, 1230, 1137, 1030, 1010, 655, 820, 770 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 8.18 (m, 2 H, 3-H, 5-H), 4.10 (qui, *J* = 7.5 Hz, 8 H, OCH_2) 3.86 (d, *J* = 22 Hz, 4 H, CH_2-P) 3.48 (m, 2 H, SO_2CH_2CH), 3.39 (dd, m, 2 H) 2.22 (sept, *J* = 6 Hz, 1 H, CH), 1.78 (m, 2 H) 1.58 – 1.43 (m, 4 H) 1.32 (t *J* = 7.5 Hz, 12 H, CH_3) 1.30 – 1.20 (m, 4 H, CH_2) 1.02 (t, *J* = 7.5 Hz, 3 H, CH_3 propyl) 0.90 – 0.83 (m, 6 H, CH_3 ethylhexyl); ^{13}C-NMR ($CDCl_3$): 10.1, 12.9, 13.9 CH3 (propyl, 2-ethylhexyl), 16.1, 16.4 (CH3 ethyl), 16.0, 22.7, 25.9, 28.5, 32.6, 33.9 (CH, CH2 propyl, ethylhexyl), 29.6 (d, *J* = 137 Hz) 29.7 (d, *J* = 135 Hz, CH2-P) 58.0, 60.2 (CH_2-SO_2), 62.6 (m, OCH_2), 131.8 (dd, *J* = 5.5 Hz, *J´*= 7.5 Hz, 132.1 *J* = 2.5 Hz, *J´* = 7.7 Hz, **C**-CH2-P) 135.2, 135.6 (C-3, C-6), 142.1 (dd, *J* = 2.5 Hz, *J`*= 6.8 Hz, 143.6 *J*= 2.6 Hz, *J´*= 6 Hz, **C**-SO_2); MS (FD) *m/z* (%): 660.3 (100) [$M^{+\bullet}$]; elemental analysis calcd (%) for $C_{27}H_{50}O_{10}P_2S_2$ (660.759): C 49.08, H 7.63, S 9.71; found: C 49.51, H 7.72, S 9.46.

*General procedure for the synthesis of OPVs **3** – **5** via Horner-olefination*

A dried 3-necked round bottom flask was equipped with a magnetic stirring bar and a dropping funnel. The dropping funnel was charged with KOtBu (336 mg, 3 mmol) in 25 mL of absolute THF. The flask contained a solution of 313 mg (2.1 mmol) 4-dimethylaminobenzaldehyde and 1 mmol of the bisphosphonate in 25 ml of abs. THF. The apparatus was immersed in an ice-water bath, flushed with argon and the base added to the starting materials while stirring. The mixtures immediately turned dark green and became fluorescent. The reaction was followed by TLC and quenched with 15 ml water (reaction time 20 min – 4 h). The bulk of the solvent was stripped off, the residue diluted with water. The solid products were isolated by filtration and washed with water, followed by methanol. Purification by recrystallization.

(*E*,*E*)-*N*-(4-{2-[4-{2-[4-(dimethylamino)phenyl]vinyl}-2-[(2-ethylhexyl)sulfonyl]-5-(propylsulfonyl)phenyl]vinyl}phenyl)-*N*,*N*-dimethylamine (**3**)

Yield:562 mg (87%) after recrystallization from dichloromethane/methanol, red powder, mp.: 193°C; IR: (KBr) 2950, 2910, 2850, 2890, 1590, 1515, 1450, 1355, 1310, 1288, 1185, 1140, 965, 945, 810 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) 8.41 (s, 1H), 8.37 (s, 1 H), 7.79 (d, *J* = 15.5 Hz, 1H), 7.78 (d, *J* = d, 15.5 Hz, 1 H), 7.48 (d, *J* = 8.7 Hz, 2 H), 7.47 (d, *J* = 8.7 Hz, 2 H), 7.17 (d, *J* = 15.5 Hz, 1H), 7.15 (d, *J* = 15.5 Hz, 1 H); 6.71 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 3.15 (m, 2 H, $SO_2C\mathbf{H}_2$-CH_2), 3.11 (d, *J* = 6 Hz, 2 H, $SO_2C\mathbf{H}_2$-CH), 1.94 (m, *J* = 6 Hz, 1 H, CH), 1.68 (m, 2

H), 1.42 (m, 2 H), 1.33 (m, 2 H), 1.13 (m, 4 H) 0.91 (t, *J* = 7.4 Hz, 3 H, CH_3 propyl), 0.77 (t, *J* = 6.7 Hz, 3 H), 0.75 (t, *J* = 7 Hz, 3 H, CH_3); ^{13}C-NMR ($CDCl_3$): 10.2, 12.9, 13.9 (CH_3), 16.3, 22.6, 25.9, 28.2, 32.5, 34.4 (CH, CH_2), 40.2 NCH_3, 56.8, 58.3 (SO_2CH_2), 112.1 *o*-CH, 117.0, 117.1, 124.3, 128.4, 128.7 *m*-CH, 135.7, 135.8, 135.9, 136.0, 138.7, 139.9 C-SO_2, 151.0 C-N; MS (FD) *m/z* (%): 651 (100) [$M^{+\bullet}$], 325.8 (8) [M^{2+}]; elemental analysis calcd (%) for $C_{37}H_{50}N_2O_4S_2$ (650.9): C 68.27, H 7.74, N 4.30; found: C 67.98, H 7.70, N 4.13.

(*E*,*E*)-2,5-bis{2-[4-(dimethylamino)phenyl]vinyl}terephthalonitrile (**4**)

Yield:310 mg (74%) after recrystallization from o-dichlorobenzene, brick-red powder, mp.: 310°C; IR: (KBr): 3010, 2880, 2840, 2790, 2215, 1585, 1518, 1465, 1438, 1358, 1308, 1180, 1160, 945, 802 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 3.02 (s, 12 H, NCH_3), 6.70 (d, 4 H, *J* = 8.6 Hz, 4 H), 7.12 (d, *J* = 16 Hz, 2 H), 7.19 (d, *J* = 16 Hz, 2 H), 7.46 (d, *J* = 8.6 Hz, 4 H), 7.94 (s, 2 H); MS (FD) *m/z* (%): 418.9 (100) [$M^{+\bullet}$], 209.7 (2) [M^{2+}]; elemental analysis calcd (%) for $C_{28}H_{26}N_4$ (418.5): C 80.35, H 6.26, N 13.39; found: C 80.04, H 6.20, N 13.02.

(*E*,*E*)-2,5-bis{2-[4-(dimethylamino)phenyl]vinyl}benzonitrile (**5**)

Yield:267 mg (68%) after recrystallization from chlorobenzene, yellow-orange powder, mp.: 272°C; IR: (KBr): 3010, 2880, 2840, 2790, 2217, 1593, 1515, 1470, 1438, 13608, 1188, 1178, 1163, 955, 942, 826, 802; ^{1}H-NMR ($CDCl_3$): 2.98 (s, 6 H, NCH_3), 3.00 (s, 6 H, NCH_3), 6.69 (d, *J* = 8.8 Hz, 4 H), 6.81 (d, *J* = 16 Hz, 1 H), 7.04 (d, *J* = 16 Hz, 1 H); 7.18/7.21 (AB-system, 2 H, *J* = 16 Hz), 7.39 (d, *J* = 8.8 Hz, 2 H); 7.46 (d, *J* = 8.8 Hz, 2 H), 7.60 (dd, *J* = 8.2 Hz, *J´*= 1.5 Hz, 1 H, 4-H), 7.64 (d, 1 H, *J* = 1.5 Hz, 6-H), 7.70 (d, *J* = 8.0 Hz, 1 H, 3-H); MS (FD) *m/z* (%): 394.0 (100) [$M^{+\bullet}$]; elemental analysis calcd (%) for $C_{27}H_{27}N_3$ (393.5): C 82.41, H 6.92,10.68 N; found: C 82.22, H 6.75, N 10.35.

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