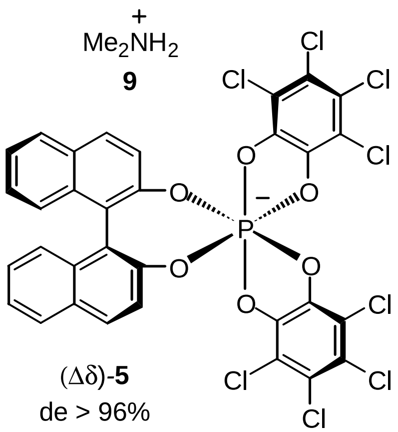


9

(Δδ)-**5**
de > 96%

Dimethylammonium bis(tetrachlorobenzenediolato)mono([1,1’]-binaphthalenyl-2,2’-diolato)phosphate(V), [9][5]:

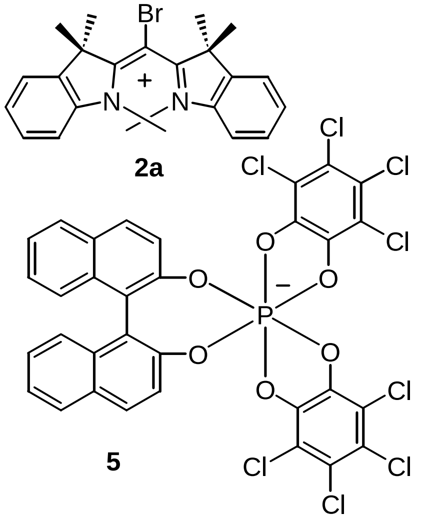
To a stirred solution of 422 mg (1.70 mmol) of tetrachlorocatechol and a catalytic amount of NH_4Cl (~2 mol%) in dry toluene (5.00 mL) under a nitrogen atmosphere was added 350 μl (1.80 mmol) of freshly distilled tris(dimethylamino)phosphine. Dimethylamine evolved. The mixture was refluxed for 15 min., then the solvent and the excess tris(dimethylamino)phosphine were removed under reduced pressure and the residue was carefully dried *in vacuo*. 286 mg (1.00 mmol) of racemic BINOL **4** and 420 mg (1.70 mmol) of *o*-chloranil were added and the mixture was dissolved in CH_2Cl_2 (10.0 mL). The dark red solution progressively lost its color and a precipitate was formed. When the color did not change anymore, the precipitate was filtered, washed successively with CH_2Cl_2, toluene and CH_2Cl_2, and dried to afford 780 mg (80 %) of the desired [$Me_2NH_2^+$][BINPHAT] salt as a single diastereomer. White solid. **M.p.** > 215-216°C (decomposition). **IR** (KBr) 3642w, 3176m, 3056m, 2809m, 2458w, 1592m, 1450s, 1390s, 1332m, 1301m, 1235s, 1075w, 992s, 952s, 828s, 783m, 753m, 674s, 618s. **^{1}H NMR** (400 MHz, DMSO-d_6) 2.53 (s, 6H), 6.56 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 3.6 Hz, 4H), 7.38 (m, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 8.15 (s broad, 2H). **^{31}P NMR** (162 MHz, DMSO-d_6) -81.8. **^{31}P NMR** (162 MHz, MeOH-d_4) -83.0. **^{13}C NMR** (100 MHz, MeOH-d_4) 35.5 (CH_3), 115.0 (C_q, d, $J_{C\text{-}P}$ = 18 Hz), 115.1 (C_q, d, $J_{C\text{-}P}$ = 20 Hz), 122.2 (C_q), 123.6 (C_q), 123.6 (CH, d, $J_{C\text{-}P}$ = 3.0 Hz), 124.3 (C_q, d, $J_{C\text{-}P}$ = 3.0 Hz), 125.2 (CH), 126.5 (CH), 128.0 (CH), 129.3 (CH), 130.4 (CH), 132.1 (C_q), 133.7 (C_q), 143.5 (C_q, d, $J_{C\text{-}P}$ = 9.1 Hz), 144.1 (C_q, d, $J_{C\text{-}P}$ = 5.3 Hz), 153.2 (C_q, d, $J_{C\text{-}P}$ = 12 Hz). **MS** (ES) (-) 807.0. **UV/Vis** (MeOH, $1.25 \cdot 10^{-5}$ M) λ_{max} (ε) 220 ($2.1 \cdot 10^5$); 301 ($2.1 \cdot 10^4$), 329 ($8.9 \cdot 10^3$). **Anal.** Calcd. for $C_{34}H_{20}NCl_8O_6P \cdot 3.44\ H_2O$: C, 44.63; H, 2.96; N, 1.53. Found: C, 44.62; H, 2.95; N, 1.72.

Salt [9][Δ-5]: Prepared according to above described using (*S*)-BINOL (286 mg, 1.00 mmol) to afford, after precipitation and filtration, 800 mg (0.87 mmol, 87%) of [**9**][Δδ-**5**]. **$[\alpha]^{20}_D$** = - 42 (*c* 0.39; MeOH). **CD** (MeOH, $7.70 \cdot 10^{-6}$ M, 20°C): λ (Δε) 229 (248), 243 (-107), 262 (29), 300 (-19).

Salt [9][Λ-5]: Prepared according to above described procedure using (*R*)-BINOL (286 mg, 1.00 mmol) to afford, after precipitation and filtration, 824 mg (0.95 mmol, 95%) of [**9**][Λλ-**5**]. **$[\alpha]^{20}_D$** = + 39 (*c* 0.34; MeOH). **CD** (MeOH, $1.25 \cdot 10^{-5}$ M, 20°C): λ (Δε) 229 (-250), 243 (122), 262 (-21), 295 (23).

General procedure for the exchange of ammonium cations for monomethinium cations

1.0 equivalent of the desired $Me_2NH_2^+$ phosphate salt was dissolved in CH_2Cl_2 or a 10:1 mixture of CH_2Cl_2 and THF and 1.0 equivalent of the tetrafluoroborate salt of the desired monomethinium cation [**2a,b**][BF_4^-] was added. The mixture was stirred for 10 min and the solvent was then removed under reduced pressure. The crude reaction mixture was purified by chromatography over basic alumina using CH_2Cl_2 as the eluent.



2a

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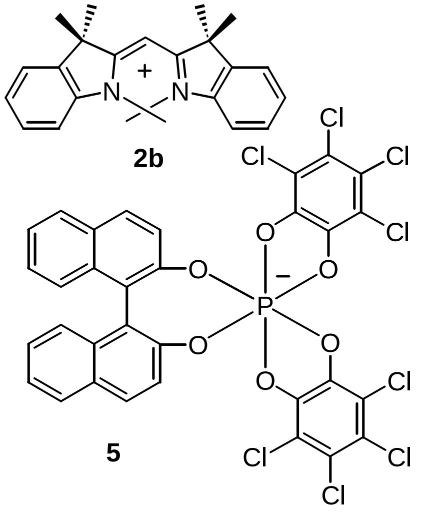
8-Bromo-bis(1,3,3-trimethylindoline-2-yl) monomethinium bis(tetrachlorobenzenediolato)mono([1,1']-binaphthalenyl-2,2'-diolato)phosphate(v), Salt [2a][5]:

Prepared according to the general procedure using 127 mg (150 μmol) of [**9**][*rac*-**5**]. Yield: 78%. Red solid. **M.p.** > 193°C (decomposition). **IR** (KBr) 2972w, 2925w, 2854w, 1727w, 1619w, 1484s, 1455s, 1385w, 1358m, 1264m, 1120w, 1010w, 994m, 954m, 822s, 785m, 752m, 6711m, 615m, 488w. ^{31}**P NMR** (162 MHz, DMSO-d_6) -81.4. ^{1}**H NMR** (400 MHz, DMSO-d_6) 1.79 (s, 6H), 1.87 (s, 6H), 2.96 (s, 6H), 6.56 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 3.8 Hz, 2H), 7340 (m, 4H), 7.49 (m, 4H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 2H). ^{13}**C NMR** (100 MHz, DMSO-d_6) 22.3 (CH_3, d, *J* = 1.6 Hz), 28.4 (CH_3), 37.7 (CH_3), 53.6 (C_q), 113.0 (C_q, d , $J_{C\text{-}P}$ = 18 Hz), 113.2 (C_q, d , $J_{C\text{-}P}$ = 20 Hz), 113.5 (C_q), 120.3 (C_q), 121.7 (C_q), 122.6 (C_q), 122.7(C_q), 122.8 (CH), 122.9 (CH), 123.0 (CH), 124.5 (CH), 126.0 (CH), 126.7 (CH), 127.3 (CH), 128.7 (CH), 129.0 (CH), 129.5 (CH), 130.3 (C_q), 130.4 (C_q), 132.2 (C_q), 141.0 (C_q), 142.1 (C_q,), 142.5 (C_q, d, $J_{C\text{-}P}$ = 8.2 Hz), 143.0 (C_q, d, $J_{C\text{-}P}$ = 5.8 Hz), 152.1 (C_q, d, $J_{C\text{-}P}$ = 12 Hz), 178.4 (C_q). **MS** (ES) (-) 807.3; (+) 410.5. **UV/Vis** ($CHCl_3$, $1.36 \cdot 10^{-5}$ M) λ_{max} (ε) 241 ($8.1 \cdot 10^{4}$), 302 ($2.5 \cdot 10^{4}$), 331 ($1.3 \cdot 10^{4}$), 513($2.4 \cdot 10^{4}$).

Salt [2a][Δ-5]: Prepared according to the general procedure using 152 mg (170 μmol) of [**9**][Δ-**5**]. Yield: 68%. Red solid. **M.p.** > 195°C (decomposition). $[\alpha]^{20}_{D}$ = + 587 (*c* 0.09 ; MeOH). **CD** ($CHCl_3$, $1.75 \cdot 10^{-5}$ M, 20°C): λ (Δε) 248 (-102), 265 (26), 294 (-16), 332 (-6.2), 528 (3.8).

Salt [2a][Λ-5]: Prepared according to the general procedure using 341 mg (400 μmol) of [**9**][Λ-**5**]. Yield: 93%. Red solid. **M.p.** > 208°C (decomposition). $[\alpha]^{20}_{D}$ = - 480 (*c* 0.09 ; MeOH). **CD** ($CHCl_3$, $1.36 \cdot 10^{-5}$ M, 20°C): λ (Δε) 249 (96), 266 (-23), 294 (17), 332 (7.1), 520 (-4.3).



2b

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Bis(1,3,3-trimethylindoline-2-yl)monomethinium bis(tetrachlorobenzenediolato)mono([1,1']-binaphthalenyl-2,2'-diolato)phosphate(v), Salt [2b][5]:

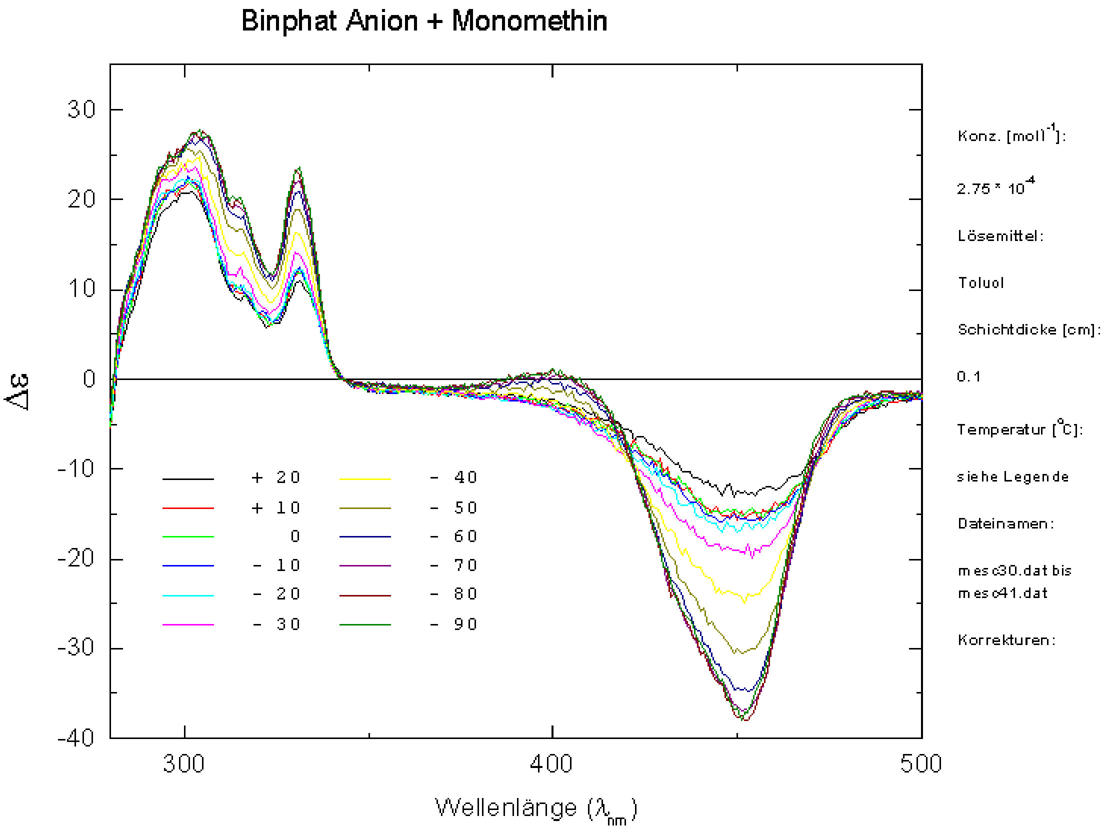
Prepared according to the general procedure using 341 mg (400 μmol) of [**9**][*rac*-**5**]. Yield: 95%. The product can be further purified by crystallization in CH_2Cl_2/EtOAc by slow diffusion of hexane. Yellow solid. **M.p.** 203-205°C. **IR** (KBr) 3054w, 2964w, 2925m, 2854w, 1727w, 1619w, 1555s, 1462s, 1385s, 1334w, 1303w, 1236m, 1125w, 1075w, 1010w, 994m, 954m, 822s, 784m, 753m, 724w, 698w, 672s, 654m, 616m, 564w, 532w, 488w. ^{31}**P NMR** (162 MHz, DMSO-d_6) -81.7. ^{1}**H NMR** (400 MHz, DMSO-d_6) 1.56 (s, 12H), 3.25 (s, 6H), 5.74 (s, 1H), 6.55 (d, *J* = 8.8 Hz, 2H), 7.26 (m, 4H), 7.33-7.38 (m, 4H), 7.46 (m, 4H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H). ^{13}**C NMR** (100 MHz, DMSO-d_6) 34.6 (CH_3), 43.8 (NCH_3), 80.8 (CH), 120.6 (CH), 120.8 (C_q, d , $J_{C\text{-}P}$ = 19 Hz), 121.0 (C_q, d , $J_{C\text{-}P}$ = 20 Hz), 128.0 (C_q), 129.5 (C_q), 130.5 (C_q), 130.6 (C_q), 130.7 (CH), 130.9 (CH), 132.2 (CH), 133.8 (CH), 134.0 (CH), 134.5 (CH), 136.4 (CH), 136.6 (CH), 137.2 (CH), 138.1 (C_q), 147.8 (C_q), 150.3 (C_q, d, $J_{C\text{-}P}$ = 8.3 Hz), 150.9

(C_q, d, $J_{C\text{-}P}$ = 6.1 Hz), 151.9 (C_q), 160.0 (C_q, d, $J_{C\text{-}P}$ = 12 Hz), 190.3 (C_q). **MS** (ES) (-) 807.1; (+) 331.2. **UV/Vis** ($CHCl_3$, $5.62{\cdot}10^{-5}$ M) λ_{max} (ε) 246 ($4.9{\cdot}10^4$), 303 ($1.7{\cdot}10^4$), 331 ($8.0{\cdot}10^3$), 439 ($2.5{\cdot}10^4$). **Anal.** Calcd. for $C_{55}H_{39}Cl_8O_6PN_2$: C, 58.02 H, 3.45; N, 2.46. Found: C, 57.74; H, 3.73; N, 2.51.

Salt [2b][Δ-5] made from (*S*)-BINOL: Prepared according to the general procedure using 256 mg (300 µmol) of [**9**][**Δ-5**]. Yield: 88%. Orange solid. **M.p.** 222-225°C. **$[\alpha]^{20}_D$** = -42 (*c* 0.18; MeOH).

Salt [2b][Λ-5] made from (*R*)-BINOL: Prepared according to the general procedure using 341 mg (400 µmol) of [**9**][**Λ-5**]. Yield: 93%. Orange solid. **M.p.** 218-222°C. **$[\alpha]^{20}_D$** = +38 (*c* 0.19; MeOH).

CD spectra (280-500 nm) of [2b][Λ-5] ($2.75{\cdot}10^{-4}$ in toluene), temperature dependence.



X-ray structural determination of (+)-[2b][5] : $[(C_{32}H_{12}O_6PCl_4)^- (C_{23}H_{28}N_2)^+]_3 (C_4H_8O_2)_4$; M_r = 3768; µ = 4.177 mm^{-1}, F(000) = 1938, d_x = 1.426 $g{\cdot}cm^{-3}$, triclinic, *P* 1 (No 1), Z = 3 (3 ions pairs and 4 EtOAc in the asymmetric unit), a = 15.542(1), b = 17.385(2), c = 19.170(2) Å, α = 65.702(7), β = 83.635(9), γ = 68.538(6)°, V = 4388.7(8)$Å^3$, from 27 reflections (36° < 2θ < 45°); Yellow prism 0.14 x 0.21 x 0.38 mm mounted on a quartz fiber with RS3000 oil. Cell dimensions and intensities were measured at 200K on a Stoe Stadi4 diffractometer with graphite-monochromated Cu[Kα] radiation (λ = 1.5418 Å), ω-2θ scans, scan width 1.05° + 0.35 tg θ, and scan speed 0.075 °/s. Two reference reflections measured every 45 min showed no variation. $-15 < h < 15$; $-17 < k < 17$; $-19 < l < 19$; 16433 unique reflections measured of wich 11323 were observables ($|Fo| > 4\sigma(Fo)$); Data were corrected for Lorentz and polarization effects and for absorption [a] (A* min , max = 1.691, 2.902). The structure was solved by direct methods using MULTAN 87 [b], all other calculations used XTAL [c] system. The chirality of the structure was refined and the Flack parameter [d] converges to x = 0.01(2). Full-matrix least-squares refinement based on F using weight of $1/(\sigma^2(Fo) + 0.0005(Fo^2))$ gave final values R = 0.063, ωR = 0.059, and S = 2.01(2) for 2070 variables and 11323 contributing reflections. Hydrogen atoms were placed in calculated positions. All non-H atoms , excepted for the EtOAc inclusion molecules, have been refined with anisotropic displacement parameters. The final difference electron density map showed a maximum of +0.68 and a minimum of -0.69 eÅ^{-3}.

References:

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