Electronic Supplementary Information for

Thermochromic Discotic 6-Oxoverdazyls

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1. Synthetic Details

Reagents and solvents were obtained commercially. Reactions were carried out under Ar, and subsequent manipulations were conducted in air. $^1$H NMR spectra were obtained at 400 MHz ($^1$H) in CDCl$_3$ and referenced to the solvent unless stated otherwise.

6-Oxoverdazyls 1[n]. General procedure. Method A. A mixture of crude tetrazane 6b[n] (0.1 mmol), anhydrous Na$_2$CO$_3$ (127 mg, 1.2 mmol), PbO$_2$ (576 mg, 2.4 mmol) in a mixture of toluene (6 mL) and MeCN (1.5 mL) was stirred overnight at rt. Additional amounts of PbO$_2$ (288 mg, 1.72 mmol) were added and stirring was continued for the next 24 h. The dark green reaction mixture was passed through a silica gel plug (CH$_2$Cl$_2$), and the crude product was purified on a silica gel column (hexane / CH$_2$Cl$_2$, 8:1) to give verdazyl 1b[n] as a dark red waxy solid in yields ~80%. The solid was recrystallized several times from AcOEt or AcOEt with a few drops of MeCN.

Method B. A mixture of partially purified tetrazane 6b[n] (0.5 mmol), K$_3$Fe(CN)$_6$ (3 mmol), 0.5 M Na$_2$CO$_3$ (10 mL), [Bu$_4$N]$^+$Br$^-$ (cat) in CH$_2$Cl$_2$ (10 mL) was stirred overnight at rt. Next portion of K$_3$Fe(CN)$_6$ (3 mmol) was added and stirring was continued until tetrazane 6b[n] is no longer detectable on TLC. The black-green CH$_2$Cl$_2$ layer was separated, dried (Na$_2$SO$_4$), solvent was evaporated and the crude product was purified as described in Method A.

1,3,5-tri-(3',4',5'-Trioctyloxyphenyl)-6-oxoverdazyl (1b[8]). Method A. UV (hexane) $\lambda_{\text{max}}$ (log $\varepsilon$) 209 (4.96), 274 (4.35), 3.44 (4.04), 486 (3.24), 614 (3.52) nm. Anal. Calcd for C$_{92}$H$_{159}$N$_4$O$_{10}$: C, 74.60; H, 10.82; N, 3.78. Found: C, 74.83; H, 10.91; N, 3.79.

1,3,5-tri-(3,4,5-Tridecyloxyphenyl)-6-oxoverdazyl (1b[10]). Method B. Anal. Calcd for C$_{110}$H$_{199}$N$_4$O$_{10}$: C, 76.20; H, 11.34; N, 3.23. Found: C, 76.35; H, 11.28; N, 3.19.
**Aldehydes 3b[n].** Aldehydes were obtained by alkylation of 3,4,5-trihydroxybenzaldehyde with appropriate alkyl bromide as described in literature\(^7,^8\) in yields about 70%. Alternatively, 3,4,5-trioctyloxybenzaldehyde (3b[8]) was obtained in 70% yield from 1,2,3-trioctyloxy-4-bromobenzene\(^9\) by lithiation with n-BuLi and subsequent treatment with DMF according to a general procedure for preparation of aldehydes 3a[n].\(^{10}\)

**3,4,5-Trioctyloxybenzaldehyde (3b[8]).**\(^7,^8\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.88 (t, \(J = 6.2\) Hz, 9H), 1.23-1.40 (m, 24H), 1.44-1.52 (m, 6H), 1.75 (quint, \(J = 7.2\) Hz, 2H), 1.83 (quint, \(J = 7.0\) Hz, 4H), 4.03 (t, \(J = 6.5\) Hz, 4H), 4.05 (t, \(J = 6.6\) Hz, 2H), 7.08 (s, 2H), 9.83 (s, 1H).

**3,4,5-Tridecyloxybenzaldehyde (3b[10]).**\(^8,^{11}\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.82 (t, \(J = 6.9\) Hz, 9H), 1.23-1.40 (m, 36H), 1.44-1.52 (m, 6H), 1.75 (quint, \(J = 7.3\) Hz, 2H), 1.83 (quint, \(J = 7.1\) Hz, 4H), 4.03 (t, \(J = 6.4\) Hz, 4H), 4.06 (t, \(J = 6.1\) Hz, 2H), 7.08 (s, 2H), 9.83 (s, 1H).

**Hydrazones 4b[n].** **General Procedure.** To a solution of crude 3,4,5-trialkylxylophenylhydrazine\(^{12}\) (2b[n], 1.3 mmol) and 3,4,5-trialkylxyloxybenzaldehyde (3b[n], 1.0 mmol) in THF (4 mL) 1 drop of AcOH was added. The mixture was refluxed for 1.5 h under Ar, cooled to rt, solvent was evaporated, and traces of AcOH removed on vacuum to give \(~80\%\) yield of crude hydrazone 4b[n] (\(~90\%\) pure), which was used for the next step without additional purification.
**3,4,5-Trioctyloxybenzaldehyde 3,4,5-trioctyloxyphenylhydrazone (4b[8]).** $^1$H NMR (400 MHz, CDCl$_3$) δ (major signals) 0.88 (t, $J$ = 6.7 Hz, 18H), 1.23-1.40 (m, 48H), 1.42-1.58 (m, 12H), 1.67-1.88 (m, 12H), 3.88 (t, $J$ = 6.6 Hz, 2H), 3.98 (t, $J$ = 6.1 Hz, 6H), 4.02 (t, $J$ = 6.4 Hz, 4H), 6.32 (s, 2H), 6.84 (s, 2H), 7.40 (s, 1H), 7.55 (s, 1H).

**3,4,5-Tridecyloxybenzaldehyde 3,4,5-tridecyloxyphenylhydrazone (4b[10]).** $^1$H NMR (400 MHz, CDCl$_3$) (characteristic signals) δ 3.89 (t, 2H), 6.33 (s, 2H), 6.84 (s, 2H), 7.41 (s, 1H), 7.56 (s, 1H).

**Carbamoyl chlorides 5b[n]. General Procedure.** To a solution of hydrazone 4b[n] (1.0 mmol) in dry CH$_2$Cl$_2$ (10 mL) pyridine (1.2 mmol) followed by triphosgene (297 mg, 1.0 mmol) were added under Ar. The mixture was stirred at ambient temperature for 4 hrs, 2% HCl was added, organic products were extracted (CH$_2$Cl$_2$), extracts dried (Na$_2$SO$_4$), and solvent evaporated. The crude product was purified on a short silica gel column (hexane / CH$_2$Cl$_2$, 2:1) to give chlorides 5b[n] as yellowish viscous oils in yields ~65%.

**3,4,5-Trioctyloxybenzaldehyde α-chloroformyl-3’,4’,5’-trioctyloxyphenylhydrazone (5b[8]).** $^1$H NMR (400 MHz, CDCl$_3$) δ 0.84-0.92 (m, 18H), 1.19-1.35 (m, 48H), 1.40-1.53 (m, 12H), 1.68-1.76 (m, 4H), 1.80 (quint, $J$ = 6.5 Hz, 8H), 3.93 (t, $J$ = 6.5 Hz, 4H), 3.97 (t, $J$ = 6.6 Hz, 2H), 3.98 (t, $J$ = 6.5 Hz, 4H), 4.03 (t, $J$ = 6.4 Hz, 2H), 6.39 (s, 2H), 6.84 (s, 2H), 7.22 (s, 1H); HRMS, calcd for C$_{62}$H$_{108}$ClN$_2$O$_7$ (M+1): m/z 1027.7840; found m/z 1027.7828.
3,4,5-Tridecyloxybenzaldehyde α-chloroformyl-3′,4′,5′-tridecyloxyphenylhydrazone (5b[10]). 1H NMR (400 MHz, CDCl$_3$) (characteristic signals) δ 6.39 (s, 2H), 6.84 (s, 2H), 7.22 (s, 1H). Molecular ion was not observed.

Tetrazanes 6b[n]. General Procedure. To a solution of carbamoyl chloride 5b[n] (1.0 mmol) in dry benzene (30 mL) a solution of freshly prepared 3,4,5-trialkylxyloxyphenylhydrazine 12 (2b[n], 1.2 mmol) and Et$_3$N (1.3 mmol) in dry benzene (10 mL) was added. The mixture was stirred for 2 h at 50 °C. A 2% solution of HCl was added, organic products were extracted (CH$_2$Cl$_2$), extracts dried (Na$_2$SO$_4$), and solvents evaporated. The crude product was purified on a short silica gel column (hexane / CH$_2$Cl$_2$, 2:1) to give partially purified tetrazane 6b[n] as a tan viscous oil or soft solid in yields ~45%. Molecular ions in MS were not observed.

2,4,6-Tri(3,4,5-trioctyloxyphenyl)-1,2,4,5-tetrazane-3-one 6b[8]. Yellow-brownish viscous oil (~60% of yield based on mass and NMR): 1H NMR (400 MHz, CDCl$_3$) δ 0.84-0.94 (m, 27H), 1.22-1.37 (m, 72H), 1.38-1.52 (m, 18H), 1.66-1.83 (m, 18H), 3.78 (t, J = 6.4 Hz, 4H), 3.90 (t, J = 6.7 Hz, 6H), 3.94 (t, J = 6.6 Hz, 8H), 4.67 (d, J = 9.1 Hz, 2H), 5.42 (t, J = 8.7 Hz, 1H), 6.69 (s, 2H), 6.84 (s, 4H).

2,4,6-Tri(3,4,5-tridecyloxyphenyl)-1,2,4,5-tetrazane-3-one 6b[10]. 1H NMR (400 MHz, CDCl$_3$) δ 0.89 (t, J = 6.6 Hz, 27H), 1.22-1.38 (m, 108H), 1.39-1.51 (m, 18H), 1.66-1.85 (m, 18H), 3.78 (t, J = 6.3 Hz, 4H), 3.91 (t, J = 6.7 Hz, 6H), 3.94 (t, J = 6.5 Hz, 8H), 4.70 (brs, 2H), 5.42 (brs, 1H) 6.70 (s, 2H), 6.85 (s, 4H).
2. Thermal analysis

Thermal analysis was performed on a TA 2920 DSC. In a typical experiment, both compounds were analyzed in multiple heating/cooling cycles with heating/cooling rates of 5 K min\(^{-1}\). The isotropic-columnar transition for 1b[10] was analyzed using variable cooling rates (Fig. S1).

**Figure S1.** Isotropic–columnar phase transition recorded on cooling for 1b[10] at various cooling rates.

**Figure S2.** Isotropic–columnar phase transition recorded for 1b[8] during 5 cycles of heating and cooling in a range of 100–135 °C at 5 K min\(^{-1}\).
3. Optical textures

![Image a) Photomicrograph of 1b[10] with crossed polarizers](image)

![Image b) Crossed polarizers and lambda plate inserted at 45 deg to the polarizer direction](image)

![Image c) No polarizers](image)

**Figure S3.** Photomicrograph of 1b[10] with crossed polarizers (a), crossed polarizers and lambda plate inserted at 45 deg to the polarizer direction (b), and no polarizers.

4. Electronic absorption spectra

UV-vis spectra for 1b[8] were recorded in spectroscopic grade hexane at concentration of $1\text{–}10 \times 10^{-6}$ M. Extinction coefficients were obtained by fitting the maximum absorbance at 260 nm against concentration in agreement with Beer’s law.

The temperature-dependent visible spectra for 1b[10] were obtained every 1 or 2 K on heating and cooling using a hot-stage mounted in a UV spectrometer. The sample was allowed to equilibrate for 3 min after each change of temperature. A plot for 1b[10] is shown in Figure S4.
Figure S4. Temperature dependent lowest energy absorption maximum of 1b[10].

5. Powder XRD measurements

X-ray diffraction experiments were performed with Bruker D8 GADDS (Cu Kα radiation, Göbel mirror, point collimator, Vantec 2000 area detector) equipped with a modified Linkam heating stage. Samples were prepared in a form of a thin film or a droplet on heated surface. The X-ray beam was incident nearly parallel to sample surface, and resulting XRD patterns were recorded as a function of temperature.

Results are shown in Figures S5–S8 and Tables S1 and S2.

Figure S5. Wide angle X-ray diffraction pattern for 1b[8] at 115 °C (a) and for 1b[10] obtained at 30 °C (b).
**Figure S6.** 2D pattern for \textbf{1b[8]} at 115 °C (left) and for \textbf{1b[10]} at 30 °C (right). Signals are indexed assuming 2D hexagonal lattice.

**Figure S7.** Temperature dependence of the position of $d_{10}$ reflection in the \textit{Col}_h phase and diffused signal in the Iso phase for \textbf{1b[10]} recorded on heating (black) and cooling (blue).

**Figure S8.** Small angle XRD pattern for \textbf{1b[10]} recorded at 50 °C (red) and at 5 °C (blue). In low temperature additional broad signal appears reflecting short-range density modulations with the periodicity twice the periodicity of (10).
Table S1. X-ray diffraction data for 1b[8].

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<th>Temp /°C</th>
<th>Phase</th>
<th>Miller indices</th>
<th>(d_{\text{meas}}/\text{Å})</th>
<th>(d_{\text{calc}}/\text{Å})</th>
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Table S2. X-ray diffraction data for 1b[10].

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6. Photoconductivity measurements and data

The charge carrier mobility was measured for 1b[8] by the TOF (time-of-flight) method using a nitrogen gas laser (Nippon Laser, 800 ps pulse at \(\lambda = 337\) nm) and a polarizing microscope with a hot stage. The cell was mounted on a handmade hot stage, and electric bias was applied by battery cells. Depending on the polarity of the applied
field (40 kV or 50 kV), positive or negative charge carriers were moving through the sample, causing displacement photocurrent, which is detected on a digital oscilloscope with a commercially available current amplifier (DHPCA-100, FEMTO). A schematic diagram of the experimental setup is shown in Figures S9 and S10 and the data in Table S3. Figure S11 shows a typical texture of a sample 1b[8] that was used for the measurements.

Thicknenss of the cells used for TOF measurements was 2.3, 5.2, and 18.6 µm and the electrodes in the thickest cell were covered with a 300 nm-thick layer of SiO₂. The cells were filled with isotropic material by capillary forces. The material was rapidly cooled to a columnar phase. Polarized optical microscopy showed a highly birefringent texture practically with no homeotropic domains. Slow cooling in magnetic field did not result in sample alignment. Optical density of the 2.3 µm sample at 337 nm was 0.72.

• Dark current measurements in a range of 25–90 °C gave the value of 10⁻¹⁴–10⁻¹² S cm⁻¹ with an activation energy of about 0.9 eV.

• Photoconductivity of 1b[8] in a 5.2 µm thick cell (area of the electrode: 0.16 cm²): 3.6×10⁻¹⁵ S cm⁻¹ at 25 °C and 6.0×10⁻¹³ S cm⁻¹ at 90 °C.

**Figure S9.** Schematic diagram of the experimental apparatus (TOF method).

**Figure S10.** Sandwich-type cell for photoconductivity measurements.
Table S3. Positive ($\mu_h$) charge mobilities in 1b[8] at 40 kV measured on cooling

<table>
<thead>
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<th>Temperature / °C</th>
<th>Mobility $\times 10^{-3}$ /cm$^2$V$^{-1}$s$^{-1}$</th>
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The estimated uncertainty of charge mobility values is about 20%, which was based on the assumed 10% of uncertainty of the cell thickness and the depth of light penetration of the sample.

Figure S11. Texture of a typical sample of 1b[8] used for photocurrent generation studies.

7. Magnetization measurements

Experiments were conducted using SQUID magnetometer (Quantum Design MPMS-XL-7T).

A small fresh sample of 1b[8] ($m = 4.73$ mg, $3.19\times10^{-6}$ mol), prepared with PbO$_2$, was placed in a polycarbonate capsule fitted in a plastic straw. The sample was subjected to heating and cooling experiments at 0.05 T in a range of temperatures of between 2 K and 400 K at a rate of 1 K min$^{-1}$.

The signal at high temperature was relatively weak and was measured once at
each temperature in the sweep mode without averaging. In the range of 40–100 K the SQUID signal changes from negative to positive (goes through 0) and magnetization $M$ could not be derived.

The diamagnetic correction was established by fitting the magnetization data to a $\chi_{\text{mol}}$ vs $1/T$ plot (Curie plot), which for an ideal paramagnet is required to go through 0. After diamagnetic correction, the Curie constant was found to be $C = \chi_{\text{mol}} T$ equal 0.317(1) cm$^3$ K mol$^{-1}$ at a temperature range 200–360 K (Figure S11). Below 200 K the plot shows increasing AF interactions (Figure S12). The established diamagnetic correction also contains correction for magnetic field strength uncertainty, which might be up to 5% at 500 Oe.

The molar susceptibility $\chi_{\text{mol}}$ was converted to dimensionless $\mu_{\text{eff}}$ according to the equation $\mu_{\text{eff}} = 2.828 \times (\chi_{\text{mol}} T)^{1/2}$ (Hoppeè, J. I. J. Chem. Ed. 1972, 49, 505) and a plot $\chi_{\text{mol}}$ vs $T$ is shown in Figure S14.

**Figure S12.** Paramagnetic molar susceptibility $\chi_{\text{mol}}$ vs $1/T$ plot after diamagnetic correction. $C = 0.317(1)$ cm$^3$ K mol$^{-1}$. H = 500 Oe

**Figure S13.** $\chi_{\text{mol}} \times T$ vs $T$ plot. H = 500 Oe.
8. Electrochemistry

Electrochemical analysis of 1b[8] was conducted under argon in dry CH₂Cl₂ containing freshly dried [Bu₄N][PF₆] (50 ºC, P₂O₅, vacuum, overnight) as the supporting electrolyte (0.1 M) and a glassy carbon working electrode with Ag/AgCl pseudo electrode as reference. The scanning rate was 0.1 V/s. Peak potentials were referenced to the Fe/Fe⁺ couple by adding small amounts of ferrocene to the solution, which was assumed to be +0.475 V versus SCE (CH₂Cl₂, 0.1 M [Bu₄N][ClO₄]).¹ A typical voltammogram for 1b[8] is shown in Figure S15 and compared to that of its sulfur analog 1a[8] recorded under identical conditions.

9. Molecular modeling and computational details

Geometry optimizations were carried out using Universal Force Field algorithm supplied with Cerius2 suite of programs. The structure of 1b[8] was set in the most
extended conformation as the initial guess, optimized and perturbed a number of times until a minimum energy was obtained. The result is shown in Figure S16.

Quantum-mechanical calculations were carried out at the UB3LYP/6-31G(d,p) level of theory using Gaussian 09 suite of programs. Geometry optimizations were undertaken using default convergence limits and without symmetry constraints. Vibrational frequencies were used to characterize the nature of the stationary points. Zero-point energy (ZPE) corrections were scaled by 0.9806.

Following general recommendations, energy for ion formation was derived as the difference of SCF energies of individual species computed using the 6-31+G(d,p) basis set at the geometries obtained with the 6-31G(d,p) basis set (single point calculations). Thermodynamic corrections were obtained using the 6-31G(d,p) basis set.

**Figure S16.** Two views of a molecule of 1b[8] optimized with UFF algorithm. All alkyl chains are in the trans conformation.

Electronic excitation energies for 1b[1] in vacuum were obtained at the UB3LYP/6-31G(d,p) level using the time-dependent DFT method supplied in the Gaussian package.

**10. Disproportionation energy**

Ionization potentials $I_p$ and electron affinities $E_a$ for 1a[1], 1b[1] and phenalenyl were calculated according to Scheme S1 and results are shown in Table S4.
2 R• \xrightarrow{\Delta E_{SCF}^1} [R^+ + R^-] \xrightarrow{\Delta E_{SCF}^2} R^+ + R^- \text{ Scheme S1}

**Table S4.** Calculated (B3LYP/6-31+G(d,p)//B3LYP/6-31G(d,p)) parameters for selected radicals in vacuum.

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<th>$I_p$ (vert) [eV]$^a$</th>
<th>$E_a$ [eV]</th>
<th>$\Delta E_{SCF}^1$ [kcal/mol]$^b$</th>
<th>$\Delta E_{SCF}^2$ [kcal/mol]$^b$</th>
<th>$\Sigma \Delta E_{SCF}$ [kcal/mol]$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a[1]</td>
<td>6.65</td>
<td>2.30</td>
<td>102.9</td>
<td>-8.8</td>
<td>94.1</td>
</tr>
<tr>
<td>1b[1]</td>
<td>6.50</td>
<td>1.84</td>
<td>107.5</td>
<td>-15.2</td>
<td>92.3</td>
</tr>
<tr>
<td></td>
<td>6.07</td>
<td>1.24</td>
<td>116.1</td>
<td>-0.7</td>
<td>115.4</td>
</tr>
</tbody>
</table>

$^a$ Calculated value scaled by 0.984 (see ref 6). $^b$ $\Delta E_{SCF}^1$ is the electron transfer energy and $\Delta E_{SCF}^2$ is the relaxation energy. $\Sigma \Delta E_{SCF}$ represents the energy of the overall disproportionation process (Scheme S1).

**11. Partial data for TD-DFT calculation (B3LYP/6-31G(d,p)) for 1b[1]**

Excitation energies and oscillator strengths:

Excited State 1: 2.028-A 2.0192 eV 614.01 nm $f$=0.0731
$<S^2>=0.778$
158A -> 159A -0.12199
158A -> 160A -0.10337
150B -> 158B 0.11329
157B -> 158B 0.96577

This state for optimization and/or second-order correction.
Total Energy, $E$(TD-HF/TD-KS) = -2095.97900447
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.075-A 2.4130 eV 513.82 nm $f$=0.0480
$<S^2>=0.827$
158A -> 159A -0.21386
151B -> 158B -0.15964
154B -> 158B -0.10715
155B -> 158B 0.11502
156B -> 158B 0.92556

Excited State 3: 2.121-A 2.4543 eV 505.17 nm $f$=0.0432
$<S^2>=0.874$
158A -> 161A -0.10493
152B -> 158B 0.14003
155B -> 158B 0.95141
156B -> 158B -0.12615

Excited State 4: 2.061-A 2.4845 eV 499.03 nm $f$=0.0016
$<S^2>=0.812$
154B -> 158B 0.98271
156B -> 158B 0.11600
Excited State 5: 2.063 eV 489.84 nm f=0.0076
\[ <S^2> = 0.814 \]
152B → 158B 0.83172
153B → 158B 0.51881
155B → 158B -0.15783

Excited State 6: 2.048 eV 481.21 nm f=0.0001
\[ <S^2> = 0.799 \]
152B → 158B -0.52395
153B → 158B 0.84328

Excited State 7: 2.049 eV 452.91 nm f=0.0069
\[ <S^2> = 0.800 \]
144B → 158B -0.13496
147B → 158B -0.31954
149B → 158B 0.12092
150B → 158B -0.23389
151B → 158B 0.85417
154B → 158B -0.10152
156B → 158B 0.15774

Excited State 8: 2.041 eV 427.75 nm f=0.0041
\[ <S^2> = 0.792 \]
152A → 159A 0.16440
158A → 159A 0.91472
158A → 165A 0.10286
150B → 158B -0.11482
156B → 158B 0.25462
157B → 158B 0.12678

Selected molecular orbitals involved in these transitions are shown in Figure S17.

α-LUMO, E = -1.11 eV

α -HOMO (SOMO), E = -5.01 eV
$\beta$-LUMO, $E = -2.76$ eV

$\beta$ -HOMO, $E = -5.52$ eV

$\beta$-HOMO–1, $E = -5.84$ eV

$\beta$ -HOMO–2, $E = -5.86$ eV

$\beta$-HOMO–3, $E = -5.94$ eV

$\beta$ -HOMO–4, $E = -5.97$ eV
Figure S17. Contours and energies of selected orbitals involved in low energy excitations in 1b[1].

12. Archive data for B3LYP/6-31G(d,p) optimizations of 1b[1]
12. References


