ELECTRONIC SUPPORTING INFORMATION

Evidence of Slow Relaxation of Magnetization in Dysprosium-Based Ionic Liquids

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Syntheses: All products were analyzed by CHN elemental analysis (Elementar Vario EL analyzer) and infrared spectroscopy (Spectrometer Perkin-Elmer Spectrum One). The water contents were analyzed using a Karl-Fischer-titrator (Metrohm 795 KFT-Titrino).

Synthesis of 1-carboxymethyl-3-methylimidazolium chloride (L1) and 1-carboxyethyl-3-methylimidazolium chloride (L2) The monocrystalls of ligand L1 and L2 were obtained by re-crystallization from water of corresponding imidazolium salts prepared according to [8] (Scheme 1):

Anal. calc. for $C_6H_9N_2Cl_1O_2$ (1): C, 40.80; H, 5.13; N, 15.86; Found: C, 40.75; H, 5.11; N, 15.80. IR (KBr), /cm⁻¹: 2942 (s, vb), 2577 (w), 2487 (mw, b), 2198 (w), 1738 (s, b), 1646 (m), 1583 (m), 1571 (m), 1440 (m, sh), 1400 (s, b), 1348 (m, sh), 1307 (m, sh), 1278 (m, sh), 1189 (vs, b), 1089 (mw, sh), 1035 (m, sh), 1020 (w, sh), 978 (s, sh), 888 (ms, sh), 854 (s), 815 (s), 775 (s, b), 682 (s), 630(s), 620 (s), 411 (m, sh); M.p.= 177 °C; Yield: ~97%.

Anal. calc. for $C_7H_{11}N_2Cl_1O_2$ (2): C, 44.10; H, 5.82; N, 14.69; Found: C, 44.08; H, 5.81; N, 14.65. IR (KBr), /cm⁻¹: 3433 (s, vb), 3108 (ms, sh), 3069 (s), 3003 (w), 2984 (w), 2712 (w), 2601 (w), 2514 (m), 2429 (mw), 1733 (s, b), 1640 (w, b), 1562 (m), 1466 (w), 1449 (w), 1435 (w), 1408 (s), 1362 (w), 1305 (w), 1229 (s), 1166 (s), 1082 (w), 1028 (w), 981 (w), 951 (w), 898 (m), 876 (m), 804 (w), 780 (m), 757 (mw), 676 (m, sh), 652 (s), 623 (w), 405 (w); Yield: ~97%.

Preparation of dysprosium containing intermediate imidazolium chlorides (ic1 and ic2)

The dysprosium oxide (3.73 g, 10 mmol) was mixed with L1 or L2 (60 mmol) in 40 ml of water. The mixture was stirred under reflux for 10 hours. The undissolved parts of oxide were filtered off from mother solution and water was evaporated under ambient conditions during next 2-3 days. The white crystalline compound appears from colorless oily product approximately after two weeks.

Preparation of $[Dy(CH_3-C_3H_3N_2-CH_2COO)_3(H_2O)_2](Tf_2N)_3(1)$

The intermediate dysprosium containing imidazolium chloride (2.40 g) was dissolved in water (10 ml) and Li[Tf₂N] (2.87 g, 10mmol) was added at room temperature. The resulting colorless hydrophobic liquid was separated after 5 days by separatory funnel. The product was left for crystallization for next 3-4 weeks. Monitoring by TLC shows the presence of small part of impurities. For further purification of compound, the solid was suspended by stirring at reflux with hexane for 1 hour and filtered off. The procedure should be repeated at least ten times (monitoring by TLC). Yield: 4.4 g (~86 %); hygroscopic, water content = 5.901 %; M.p.: 74 °C; T_{dec}(start) = 317 °C; Anal. calc. for C₂₄H₂₈N₉Dy₁F₁₈S₆O₂₀ (**2**): C, 19.75; H, 1.93; N, 8.64; Found: C, 19.74; H, 2.02; N, 8.56. IR (KBr), /cm⁻¹: 3443 (b, w), 3159 (b, w), 1570 (s), 1458 (m, sh), 1412 (m, sh), 1336 (s, sh), 1323 (s, sh), 1232 (m, sh), 1180 (vs), 1128 (vs), 1058 (vs), 978 (mw, sh), 940 (w, sh), 856 (mw), 786 (m, sh), 739 (m, sh), 712 (m, sh).

Preparation of [Dy(CH₃-C₃H₃N₂-CH₂COO)₃(H₂O)](PF₆)₃·2H₂O (2)

The intermediate dysprosium containing imidazolium chloride (2.40 g) and KPF₆ (2.87 g, 10mmol) were dissolved in water (25 ml) and refluxed for 3h. After the slow evaporation at ambient temperature, thin crystals appear on the wall of glass and the mixture of thin (**3**) and rectangular colorless (KCl) crystals on the bottom. Thin crystals were collected and re-crystallized several times from water/EtOH solution. Yield: 0.49 g (~14 %); M.p. (glass transition point): 113 °C; $T_{dec}(start) = 242$ °C; Anal. calc. for $C_{18}H_{30}N_6Dy_1F_{18}P_3O_9$ (**3**): C, 20.17; H, 2.82; N, 7.84; Found: C, 20.11; H, 2.79; N, 7.80.IR (KBr), /cm⁻¹: 3649 (w), 3600 (b, w), 1626 (m), 1591 (m), 1451 (w, sh), 1411 (m, sh), 1393 (mw, sh), 1349 (w), 1309 (w, sh), 1172 (m, sh), 1117 (w), 938 (w), 819 (vs, sh), 790 (vs, sh).

Preparation of $[Dy(C_2H_5-C_3H_3N_2-CH_2COO)_3(H_2O)_2](Tf_2N)_3(3)$

The intermediate dysprosium containing imidazolium chloride (2.50 g) was dissolved in water (10 ml) and Li[Tf₂N] (2.87 g, 10mmol) was added at room temperature. After the evaporation at ambient temperature, yellowish oil appear on the bottom of glass together with rectangular colorless (KCl) crystals. After decantation, the oil was suspended by stirring at reflux with hexane for 1 hour and filtered off. The procedure should be repeated about ten times (monitoring by TLC). Yield: 1.6 g (~32 %); viscous liquid at room temperature; Anal. calc. for $C_{27}H_{34}N_9Dy_1F_{18}S_6O_{20}$ (3): C, 21.60; H, 2.28; N, 8.40; Found: C, 21.74; H, 2.33; N, 8.46. IR (KBr), /cm⁻¹: 3547 (b, m), 3162 (b, w), 2989 (b, w), 2902 (w), 1630 (b, s), 1569 (w), 1452 (ws), 1412 (m), 1342 (s), 1323 (s), 1184 (vs), 1128 (vs), 1052 (vs), 980 (w), 843 (b, w), 792 (m), 766 (w), 742 (m), 692 (mw), 655 (w).

General procedure for synthesis of ethyl 2-methyl-4-(2-oxo-2,3-dihydro-1*H*-3-indolyl)-5-phenyl-1*H*-3-pyrrolecarboxylate (5)

Ethyl acetoacetate (0.001 mol), catalyst (10 mg) and ammonium acetate (0.0025 mol) to the suspension of 3-(2-oxo-2-phenylethylidene)indolin-2-one (0.001 mol) in dry EtOH (4 ml) was added at vigorously stirring. After about 30min, stirring at reflux (monitoring by TLC) the product was filtered. Analytical sample with m.p. 317-318 oC has been obtained by recrystallization from EtOH. IR (KBr), /cm-1: 3348, 3208, 1702, 1667, 1465, 1101, 698; Anal. calc. for $C_{22}H_{20}N_2O_3$ (5): C, 73.32; H, 5.59; N, 7.77. Found: C, 73.26; H, 5.55; N, 7.70. ¹H NMR (DMSO d-6, 400.13 MHz), δ , ppm, J/Hz: 0.86 t (3H, Me, J 8.0 Hz), 2.51 s (3H, Me), 3.73 q (2H, CH2, J 8.0 Hz), 6.82-7.55 m (9H, arom), 10.34 s (1H, NH), 11.63 s (1H, NH). ¹³C NMR (DMSO d-6,100.61 MHz), δ , ppm: 178.9, 164.5, 143.4, 137.1, 132.3, 132.1, 129.3, 128.3, 128.2, 127.8, 127.4, 122.9, 121.3, 114.2, 110.2, 109.2, 58.3, 45.2, 14.4, 13.6.

Oxindoles as well as pyrroles are one of the most prevalent heterocyclic compounds, which are present as the basic cores in many potent pharmaceutical compounds, natural products and various kinds of useful materials.^[15] Multicomponent reactions continue to be the center of attention for the preparation compounds since three or more molecular building blocks can be combined in one target substance.^[25] Extending work on the synthesis of hybrids of both heterocyclic moieties of the title compounds, these were tested as new catalysts to a known^[35] synthesis of 2-pyrrolo-3'-yloxindole (**5**) by a sequential Michael addition followed by Paal–Knorr condensation.

Scheme 1. Synthesis of 2-pyrrolo-3'-yloxindole (5).



The functionalized imidazolium salts 1-3 assisted three-component coupling of 3-phenacylideneoxindole (4a), ethyl acetoacetate (4b) and ammonium acetate (4c), was tested. In our case use of ionic liquids 1-3 (10 mg, ~0.15 mol%) catalyze a one-pot reaction with ca 58-99% yield (test with 10 cycles). It should be noted that by increasing the molar ratio of each compound up to 2 mol% only a small change in percentage was seen on. The high purity, good yields and easy separation of 5 by simple filtration, prompted us to investigate the reuse and recycling of our catalysts. After removal of 5, the remainder was directly recycled in subsequent runs. As shown in table S1, the catalysts can be reused at least ten times without significant loss of activity.

Table S1: The recycle of catalysts in synthesis of ethyl 2-methyl-4-(2-oxo-2,3-dihydro-1*H*-3-indolyl)-5-phenyl-1*H*-3-pyrrolecarboxylate.

	Number of cycles/Yield [%]									
Catalyst	1	2	3	4	5	6	7	8	9	10
1	97.8	96.4	94.3	94.0	92.8	91.6	90.0	80.0	76.1	58.3
2	95.4	94.6	93.0	90.8	88.3	88.8	86.1	86.4	85.9	86.0
3*	99.0	96.3	94.8	94.1	93.8	92.0	91.4	91.2	88.8	87.3
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* - after 1 hour.

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- [2S] M. A. P. Martins, C. P. Frizzo, D. N. Moreira, N. Zanatta, H. G. Bonacorso, Chem. Rev. 2008, 108, 2015–2050.

[3S] G. Shanthi, R. T. Perumal, Tetrahedron Lett. 2009, 50, 3959–3962.



Figure S1: Thermograms of $[Dy(cmmim)_3(H_2O)_2](Tf_2N)_3$ (1) and $[Dy(cmmim)_3(H_2O)](PF_6)_3 \cdot 2H_2O$ (2). Loss of 1.8% of mass up to 116 °C in case of 2 corresponds to the elimination of one lattice water molecule.



Figure S2: DSC curves of [Dy(cmmim)₃(H₂O)₂](Tf₂N)₃ (1) (down) and [Dy(cmmim)₃(H₂O)](PF₆)₃·2H₂O (2) (up).



Figure S3: Crystal packing of complex **1**, viewed along the c-axis (i.e. in the direction of the polymeric chains). Dy violet, O red, N blue, C grey, S yellow, F green; C-H…O interactions shown as red dotted lines, C-H…F as green dotted lines.



Fig. S4. A fragment of the cationic polymer in **2** (carboxylate bridges in orange, hydrogen bonds as pink dotted lines). Symmetry operations: ' = x, $-y+\frac{1}{2}$, $z-\frac{1}{2}$; '' = x, $-y+\frac{1}{2}$, $z+\frac{1}{2}$; '' = x, y, z-1.



Figure S5: Crystal packing of complex **2**, viewed along the c-axis (i.e. in the direction of the polymeric chains). Dy violet, O red, N blue, C grey, P brown, F green; C-H…O interactions shown as pink dotted lines, C-H…F as green dotted lines.



Figure S6: (Left) Temperature dependence of dc magnetic susceptibility of complex 1. (Right) Field dependence of magnetization of complex 1.



Figure S7: (Left) Temperature dependence of dc magnetic susceptibility of complex 2. (Right) Field dependence of magnetization of complex 2.



Figure S8: Temperature dependence of ac magnetic susceptibility of complex 1 at a frequency of 1000 Hz.



Figure S9: Temperature dependence of ac magnetic susceptibility of complex 2 at a frequency of 1000 Hz.



Figure S10: Frequency dependence of ac magnetic susceptibility of complex 1 under different external dc fields.



Figure S11: Frequency dependence of ac magnetic susceptibility of complex 2 under different external dc fields.



Figure S12: Frequency dependence of ac magnetic susceptibility of complex 1 at indicated temperatures under a dc field of 2000 Oe.



Figure S13: Frequency dependence of ac magnetic susceptibility of complex 1 at indicated temperatures under a dc field of 5000 Oe.



Figure S14: Frequency dependence of ac magnetic susceptibility of complex 2 at indicated temperatures under a dc field of 1500 Oe.



Figure S15: Arrhenius semilog plots of the relaxation time, τ vs 1/T of complexes 1 and 2 from ac susceptibility measurements under a static field. The solid lines represent a linear fit in the thermally activated range of temperature. The parameters are discussed in the text.

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Figure S16: Temperature dependence and frequency dependence of ac magnetic susceptibility of complex 3 under external dc field 1500Oe



Figure S17: Temperature dependence of dc magnetic susceptibility (left) and field dependence of magnetization (right) for complex 3.