Electronic Supplementary Material (ESI) for ChemComm.

N,N′-Dialkyl-N,N′-diaryl-1,10-phenanthroline-2,9-dicarboxamides as donor ligands for separation of rare earth elements with a high and unusual selectivity. DFT computational and experimental studies.

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Electronic Supplementary Information (ESI)

Calculations details.

The geometries of ligand IV and its complexes (IV)Ln(NO_3)$_3$ were completely optimized for the gas phase conditions by first-principles DFT (GGA PBE). It is well known that the results of calculation of metal complexes depend very strongly on the basis sets used and on the methods of taking into account the relativistic effects. In order to improve the accuracy and reliability of the results, we used the scalar-relativistic theory and relativistic full-electron basis set consisting of: {3,2,1}/{8,4,2} for H; {4,3,2,1}/{12,8,4,2} for C, N, and O; {5,4,2,1}/{19,13,5,2} for Cl; {10,9,7,3,1}/{33,32,22,12,5} for La; {10,9,7,4,1}/{33,32,22,17,4} for Lu; {9,8,6,3,1} /{30,29,20,14,6}, for all others lanthanides. The stationary points were identified by an analysis of Hessians. The statistical formulas for rigid rotator and harmonic oscillator were used for the calculation of the thermodynamic functions (Gibbs energy, *G*) at 298.15 K. Atomic charges values were calculated according to Hirschfeld (Hirshfeld, F.L. *Theoret. Chim. Acta (Berl.)*, 1977, *44*, 129.).

The search for a global minimum on the PES of conformationally labile molecules (among which are the ligand and complexes under study) is difficult because of the presence of many local minima on the PES with a small energies differences (1–3 kcal/mol) corresponding to diverse conformations with different values of planar and/or dihedral angles. Therefore, in all cases, the calculations were performed using several starting geometries of the symmetric and asymmetric types. The conformation with a minimum total energy was chosen as a final one. All calculations were performed at the MBC-100к Cluster of the Joint Supercomputer Center (JSCC, Moscow) using the PRIRODA code developed by D.N. Laikov (Laikov, D.N.; Ustynyuk Yu.A.; *Rus.Chem. Bul.,* 2005, *54*, 820).

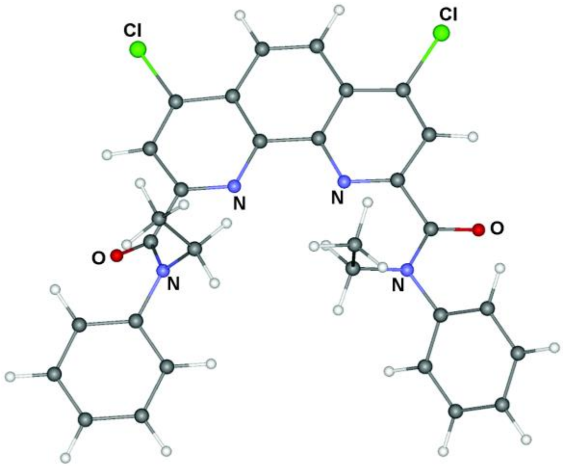

Fig.1.The non-planar twisted conformation of N,N′-Diethyl-N,N′-diphenyl-4,7-dichloro-1,10-phenanthroline-2,9-dicarboxamide.

Cartesian coordinates for diamide (V).

6	0.13249275	-2.71867031	2.27172466
6	1.43089460	-2.72305292	1.46914221
6	2.34868877	-3.73971259	1.81734364
6	3.50262556	-3.85600648	1.07721806
6	3.72895159	-3.01034135	-0.04088691
6	2.70460291	-2.05411644	-0.32491788
7	1.59775034	-1.90674470	0.43624301
6	0.86561256	1.40205386	-3.30068420
8	0.86647902	1.70976181	-4.48917091
7	-0.10725766	1.83306442	-2.42280982

6	-0.07288542	1.69515992	-0.94780938
6	-1.14695312	2.68161065	-2.94670014
7	-0.45901873	-1.51434056	2.58842656
17	4.68442948	-5.06889823	1.51958065
6	4.89331013	-3.07919434	-0.86098934
8	-0.33327163	-3.81105399	2.57732373
6	0.23131055	-0.20827182	2.48782077
6	-1.71338068	-1.52270907	3.29240323
1	2.12052985	-4.40997511	2.64556575
1	-1.12038222	1.65718214	-0.61004577
6	0.65377440	2.86184898	-0.27508449
6	1.03325463	0.12275219	3.74748001
1	-0.54393166	0.55509573	2.32123146
1	0.86660429	-0.23333978	1.59407935
6	-2.77960602	-0.77305841	2.78082698
6	-1.88118027	-2.23892786	4.48361647
6	-3.10304036	-2.19442189	5.15566642
1	-1.05843576	-2.83988800	4.87161955
6	-3.99677204	-0.72615701	3.46110536
1	-2.65587046	-0.23721671	1.83618107
1	-3.22576379	-2.75745982	6.08422075
6	-4.16246735	-1.43658332	4.65170897
1	-4.82284968	-0.14014229	3.05081117
1	0.40154316	0.73506003	-0.71180299
6	-0.85130638	3.90906385	-3.55029211
6	-2.48023763	2.27934120	-2.81195947
6	-1.88504716	4.72734793	-4.00598362
1	0.18973345	4.21181374	-3.67205871
6	-3.51149268	3.10376914	-3.26454094
1	-2.70490953	1.30812688	-2.36327906
1	-1.64643992	5.68398246	-4.47738776
6	-3.21687873	4.33079827	-3.86194397
1	-4.54945944	2.77855880	-3.15915321
1	0.60930157	2.74861955	0.82062853
1	1.71406918	2.88711235	-0.57226905
1	0.19339773	3.82705533	-0.53837452
1	1.49207023	1.11991563	3.64844015
1	0.38776352	0.12776317	4.63962794
1	1.83988106	-0.61084962	3.90455971
1	-4.02348381	4.97496716	-4.22031272
1	-5.11682858	-1.40420514	5.18276250
6	2.86166615	-1.18306286	-1.48717752
7	1.86885566	-0.31245134	-1.76598344
6	4.05008476	-1.29142222	-2.27398057
6	1.98932014	0.47639930	-2.82448875

6	5.05126387	-2.24698809	-1.93244434
1	5.65913285	-3.81621772	-0.61391894
6	4.14270777	-0.41342978	-3.38609969
17	5.56010388	-0.44191035	-4.41361898
6	3.11898769	0.45736673	-3.67639274
1	5.94616481	-2.30640297	-2.55401132
1	3.12934335	1.11117248	-4.54769010

Cartesian coordinates for complex [(V)Gd(NO$_3$]

6	-0.00146073	-2.76987191	1.82502103
6	1.43534934	-2.36046319	1.57271623
6	2.55091482	-2.85221229	2.27843080
6	3.81524103	-2.51770465	1.82989778
6	3.98295308	-1.68351017	0.69516125
6	2.78144369	-1.25209882	0.06688416
7	1.55383472	-1.59746523	0.48990879
6	0.32213822	0.95854314	-3.31008524
8	-0.49918280	0.04274652	-3.13891706
7	0.03847772	2.06369098	-4.04642993
6	-1.28285922	2.11767977	-4.72849861
6	0.75106006	3.29714249	-3.87800827
7	-0.41054652	-3.10732619	3.07514911
17	5.20789944	-3.13704170	2.67634589
6	5.24032906	-1.27181860	0.15816269
8	-0.74922451	-2.84405847	0.83616044
6	-1.78413963	-3.65915230	3.22596738
6	0.23799859	-2.60572644	4.25213373
1	2.42761612	-3.48589893	3.15595040
64	-0.72291481	-1.01668387	-0.87879609
1	-1.14114543	2.73250596	-5.63131543
6	-2.38774398	2.68445364	-3.84007928
6	-2.84447529	-2.57461315	3.40122661
1	-1.75407840	-4.33322367	4.09655741
1	-1.98482053	-4.25378112	2.32321922
6	0.59511862	-3.48626015	5.28170974
6	0.47369021	-1.23037231	4.38052010
6	1.10123476	-0.74760291	5.53046062
1	0.15185306	-0.55093667	3.58256372
6	1.20997450	-2.99038202	6.43096869
1	0.40277155	-4.55687745	5.17234548
1	1.28596180	0.32493878	5.62931192
6	1.47001617	-1.62206596	6.55470857
1	1.49330145	-3.67767539	7.23184873

1	-1.52147044	1.08864898	-5.03340077
6	0.91412159	3.83347744	-2.59373802
6	1.24377589	3.97761002	-4.99922135
6	1.60406247	5.03705879	-2.43681671
1	0.48785418	3.30775224	-1.73126720
6	1.92045520	5.18526686	-4.83070311
1	1.10736004	3.55162502	-5.99677450
1	1.73184844	5.45413895	-1.43484170
6	2.10747399	5.71370637	-3.54968885
1	2.30938093	5.71349200	-5.70464253
1	-3.32017734	2.74334029	-4.42364810
1	-2.56805500	2.02724800	-2.97564812
1	-2.13704167	3.69717976	-3.48818380
1	-3.82358657	-3.05435559	3.55808813
1	-2.62711982	-1.94120435	4.27522296
1	-2.91309892	-1.94771300	2.49901729
1	2.63934885	6.65955064	-3.42166413
1	1.95324015	-1.23758770	7.45613681
6	2.85518226	-0.40272421	-1.10336638
7	1.68939435	-0.03582387	-1.66153859
6	4.12793689	-0.01322689	-1.60622614
6	1.70628234	0.76034965	-2.72665680
6	5.30999984	-0.46922246	-0.94770538
1	6.15229138	-1.61360093	0.65035623
6	4.10433814	0.81276399	-2.75898190
17	5.59645327	1.33900311	-3.49124440
6	2.90346611	1.20951432	-3.31765421
1	6.27816746	-0.16354670	-1.34765255
1	2.89084788	1.85151342	-4.19769722
7	-3.55682013	-0.56846202	-0.73138971
8	-2.80569874	-0.03482314	-1.64602828
8	-4.75548978	-0.38352578	-0.67252161
8	-2.91688274	-1.31624970	0.11519849
7	-0.49935714	-3.32152373	-2.53883492
8	0.54141119	-2.71559808	-2.03251208
8	-1.63757852	-2.79291026	-2.22704609
8	-0.39564996	-4.30285249	-3.24522067
7	-0.40537487	1.33482021	0.84948923
8	-0.47144120	1.42559927	-0.44133999
8	-0.18423933	2.29763308	1.56318155
8	-0.58440017	0.14265491	1.32448074

Extraction procedure.

We determined the distribution coefficients *D* for Ln^{3+} ions between the aqueous and organic phases at different concentrations of nitric acid and various concentrations of ligand **V** in *m*-nitro(trifluoromethyl)benzene (F3). All extraction experiments were carried out at 25^0C in 5 mL polypropylene vials, each of which were charged with the organic phase (2 mL) and an aqueous solution (2 mL) of suitable composition. Preliminary experiments showed that the extraction equilibrium is achieved after 5 minutes of vigorous agitation, and this mixing time was maintained constant during all experiments. The organic phase was previously saturated with nitric acid by contacting the solution with the desired concentration of nitric acid containing no metals. The equilibrium aqueous and organic phases were separated by centrifugation and then both were sampled for analysis.

The lanthanide concentrations were determined on a Varian 725 -ES (Australia) ICP-OES optical emission spectrometer. The starting solution contained nitric acid and metal cations from lanthanum to lutetium (the concentration of each metal is ~ 10^{-4} mol/L). All experiments were performed in duplicate. The spectral measurement error for determination of lanthanides in solutions under study is ~10-15 %.