Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Hydrophobic Cyclic Dipeptides as M^+/Cl^- Carriers

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Table of contents

General methods

All reagents were purchased from commercially available suppliers and used directly unless stated otherwise. Oven-dried glassware was used for all air-sensitive reactions. Air-sensitive reagents and solvents were transferred using oven-dried syringe under a nitrogen atmosphere. Dichloromethane (DCM), *N, N*-dimethylformamide (DMF) and methanol were distilled by using the standard procedures. Boc-anhydride, dioxane, benzyl bromide, HBTU (2-(1H-benzo[d][1,2,3]triazol-1-yl)-1,1,3,3-tetramethylisouronium), diisopropyl ethyl amine (DIEA), trifluoroacetic acid (TFA), 4-dimethylaminopyridine (DMAP), lithium hydroxide (LiOH) were purchased from spectrochem and used without further purification. 8-hydroxypyrene-1,3,6 trisulfonic acid, trisodium salt (HPTS) and *N, N'*-dimethyl-9,9'-biacridinium dinitrate (Lucigenin) were purchased from Sigma-Aldrich and used without further purification. Egg yolk phosphatidylcholine (EYPC) and 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) lipids were purchased from Avanti Polar Lipids as a solution in chloroform (25 mg/mL). HEPES buffer, Triton X-100, sephadex G-50, cationic and anionic salts were purchased from Merk. Mini extruder and polycarbonate membrane purchased from Avanti Polar Lipids was used to prepare the Large unilamellar vesicles (LUV). Analytical thin layer chromatography (TLC) was performed on MERCK pre-coated silica gel 60 F254TLC plates. Compounds were visualized using UV light and ninhydrin. Flash column chromatography was performed using silica gel (180 – 200 mesh).

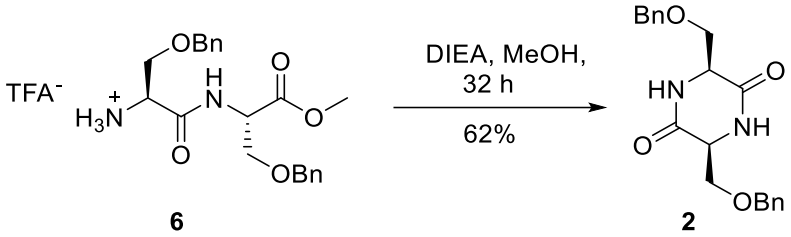
NMR spectra were recorded in deuterated solvents using Bruker Avance 400 and 500 MHz spectrophotometers. The NMR spectra were referenced using residual solvent peaks as the standard. Chemical shifts are denoted in parts per million (δ), coupling constants (*J*) are reported in Hertz (Hz), and spin multiplicities are reported as singlet (s), doublet (d), doublet of doublet (dd) triplet (t) and multiplet (m). High resolution mass measurements were carried out using Micromass Q-ToF ESI instrument using direct inlet mode.

EYPC (and DPPC wherever stated) lipid were used to prepare the vesicles using a mini extruder. Deionized water was used to prepare the buffer and vesicles. Vesicles were prepared in suitable buffer or salt at room temperature. pH of the buffer was checked using the Laqua pH meter. HCl/MOH (NaOH, KOH, LiOH, CsOH and RbOH) were used to adjust the required pH of the buffer. Fluorescence spectra were recorded a using Fluoromax-4 Horiba Scientific instrument equipped with an injector port and a magnetic stirrer. HEPES/NaCl (10 mM/100 mM) buffer solution was used for the HPTS assay and the pH of the buffer was adjusted using a Laqua pH meter (Laqua pH 1200 from Horiba Scientific). pH 7 was used for vesicle

preparation and a buffer having pH 7 or 8 as required was used as external buffer (extravesicular buffer). Lucigenin assays were prepared in the aqueous solution of $NaNO_3$ (225 mM). Origin Pro 9.1 software was used to process the fluorescence data.

Synthesis of Benzene ether DKP 2

Scheme S1



6 **2**

To a solution of dipeptide **6**[1] (0.126 g, 0.253 mmol, 1 equiv) in MeOH (2 mL) at 0 **º**C was added DIEA (0.176 mL, 1 mmol, 4 equiv). The reaction mixture was allowed to stir at 0 °C for 2 h and additionally at room temperature for 32 h. Subsequently, the solvent was removed in vacuo and the ethyl acetate (15 mL) was added to the residue. The solution was sequentially washed with 5% HCl (2 × 15 ml) and saturated sodium bicarbonate solution (2 × 15 mL). The organic layer was dried over the sodium sulphate, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (3% MeOH/DCM) to afford 0.055 g of dipeptide **2** (62%) as a white powder. **^{1}H NMR** (400 MHz, $CDCl_3$, 25°C): δ = 7.38 – 7.27 (10H, Ar*H*), 6.30 (s, 2H, CON*H*), 4.45 (dd, *J* = 14.4, 11.6 Hz, 4H, CH_{2Bn}), 4.23 – 4.19 (m, 2H, HCH_{ser}), 3.84 (dd, *J* = 9.6, 3.2 Hz, 2H, HCH_{ser}), 3.66 (app t, *J* = 8.5 Hz, 2H, CH_{ser}). 2.17 (acetone), 1.62 (water). **^{13}C NMR** (125 MHz, $CDCl_3$, 25°C): δ = 165.7, 137.2, 128.7, 128.2, 128.1, 73.7, 71.3, 55.2. **IR** (thin film): *υ* 3873, 3586, 2812, 1682, 1348, 1197, 897, 796, 603. **HRMS** (**ESI/Q-TOF)** m/z: $[M+Na]^+$ calcd. for $C_{20}H_{22}N_2NaO_4$ 377.1472; found 377.1477.

Ion transport activity of norbornene ester DKP 1-5 using HPTS assay

Vesicle preparation[2]

1mL of EYPC lipid in chloroform (25 mg) was taken in a 10 mL round bottom flask. Chloroform was removed using a stream of nitrogen and further kept in vacuo for 3 h at 0 ºC to form a dried thin lipid film. The lipid film was hydrated by HPTS dye (1 mL of 0.5 mM HPTS, 100 mM NaCl, 10 mM HEPES in water) at pH 7. The resulting mixture was allowed to

stir at room temperature for 1 h and was then subjected to three freeze-thaw cycles. The suspension was extruded 19 times through 0.1 µm polycarbonate membranes using a mini-extruder obtained from Avanti Polar Lipids. The extra-vesicular dye was removed by size exclusion chromatography using Sephadex G-50 (eluent: HEPES-NaCl buffer at pH 7.0 (100 mM NaCl, 10 mM HEPES)). The milky white vesicle solution was collected and diluted to 3.2 ml to get the 10 mM lipid stock solution.

The HPTS assay for comparative ion transport activity of DKP 1-5

30 µL of HPTS containing vesicle was added to 1970 µL of KCl:HEPES buffer (10 mM HEPES, 100 mM KCl, pH 8) in a fluorescence cuvette to generate pH/ion gradient across lipid bilayer. This cuvette was placed on the fluorescence instrument equipped with magnetic stirrer. For the fluorescence measurement excitation and emission wavelength used were 460 nm and 510 nm, respectively. A solution of DKP **1 - 5** (7.55 µM, 5 mol%)) in THF (10 µL) was added at t = 50 s. At t = 250 s, Triton-X (20%, 20 µL) was added to lyse the vesicle and achieve the maximum fluorescence intensity. The maximum intensity obtained was used to normalize the fluorescence intensity (Figure S1).

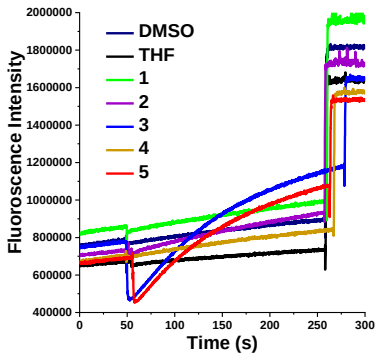


Figure S1. Raw data of K^+ transport of DKP **1-5**

Rate constant calculations

Curve obtained after addition of DKP and before addition of Triton-X was fitted to Equation (S1) using Origin Pro 9.1 software, where k corresponds to rate constant for ion transport and t correspond to time.

$$\text{Rate} = A.e^{-k.t} + C \qquad \text{S1}$$

Model	Exponential	
Equation	y = y0 + A*exp(R0*x)	
Plot	THF	5
y0	0.16455 ± 0.00416	0.6972 ± 7.55472E-4
A	-0.16581 ± 0.00401	-0.69945 ± 6.30485E-4
R0	-0.00328 ± 1.12702E-4	-0.00845 ± 1.92506E-5
Reduced Chi-Sqr	8.77644E-6	1.12685E-5
R-Square (COD)	0.98368	0.99957
Adj. R-Square	0.98366	0.99957

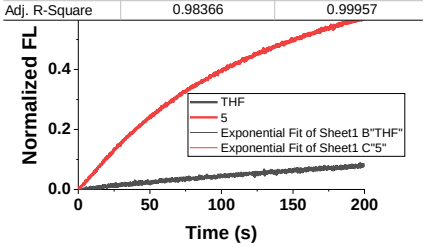


Figure S2. Representative fit curve of DKP **5**

HPTS assay for ion selectivity based on dual gradient

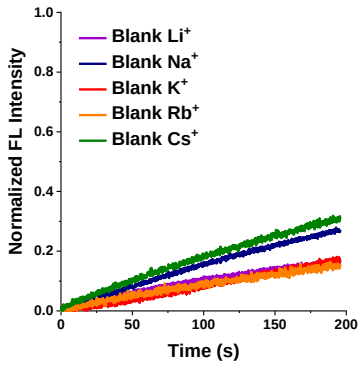
Assay to study effect of external cation

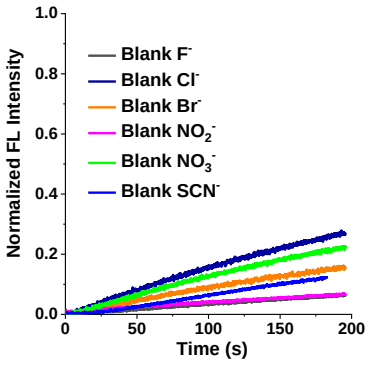
The vesicle preparation and assay procedure described above was carried out with the only change that 100 mM MCl buffer (10 mM HEPES, 100 mM MCl, (M = Li^+, Na^+, K^+, Cs^+, Rb^+), pH 8) was used in the extravesicular buffer instead of KCl and 10.57 µM (7 mol%) DKP concentration used.

Assay to study effect of external anion

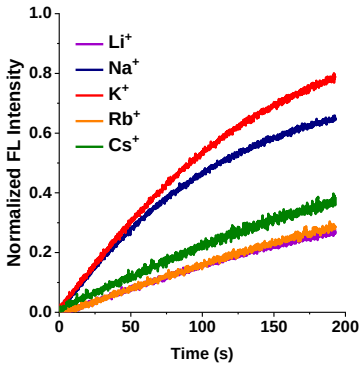
The assay procedure described above was carried out with the only change that 100 mM NaX (X = F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SCN^-, pH = 8.0) was used in the extravesicular buffer instead of MCl.

a) b)

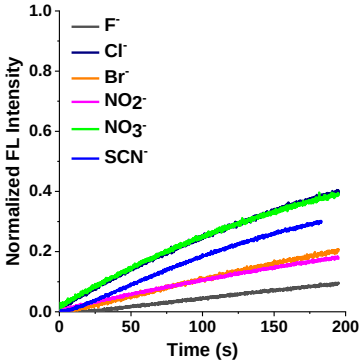




c)

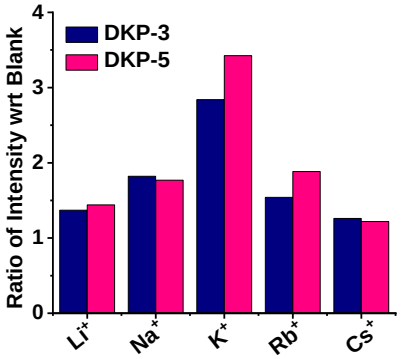

Normalized FL Intensity
Time (s)
Li+
Na+
K+
Rb+
Cs+

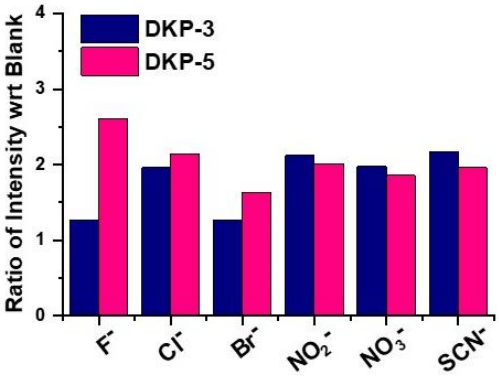
d)


Normalized FL Intensity
Time (s)
F-
Cl-
Br-
NO2-
NO3-
SCN-

e)

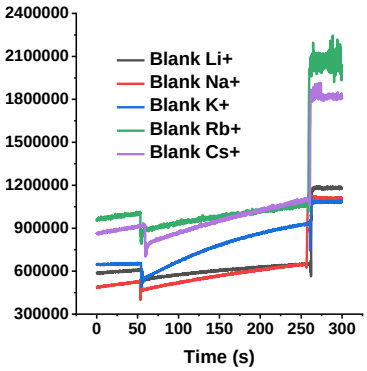
f)

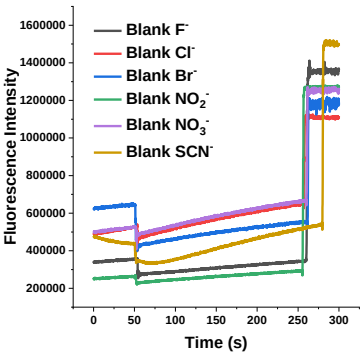

Ratio of Intensity wrt Blank
DKP-3
DKP-5
Li+
Na+
K+
Rb+
Cs+


Ratio of Intensity wrt Blank
DKP-3
DKP-5
F-
Cl-
Br-
NO2-
NO3-
SCN-

g)

h)


Blank Li+
Blank Na+
Blank K+
Blank Rb+
Blank Cs+
Time (s)


Blank F-
Blank Cl-
Blank Br-
Blank NO2-
Blank NO3-
Blank SCN-
Fluorescence Intensity
Time (s)

i)

j)

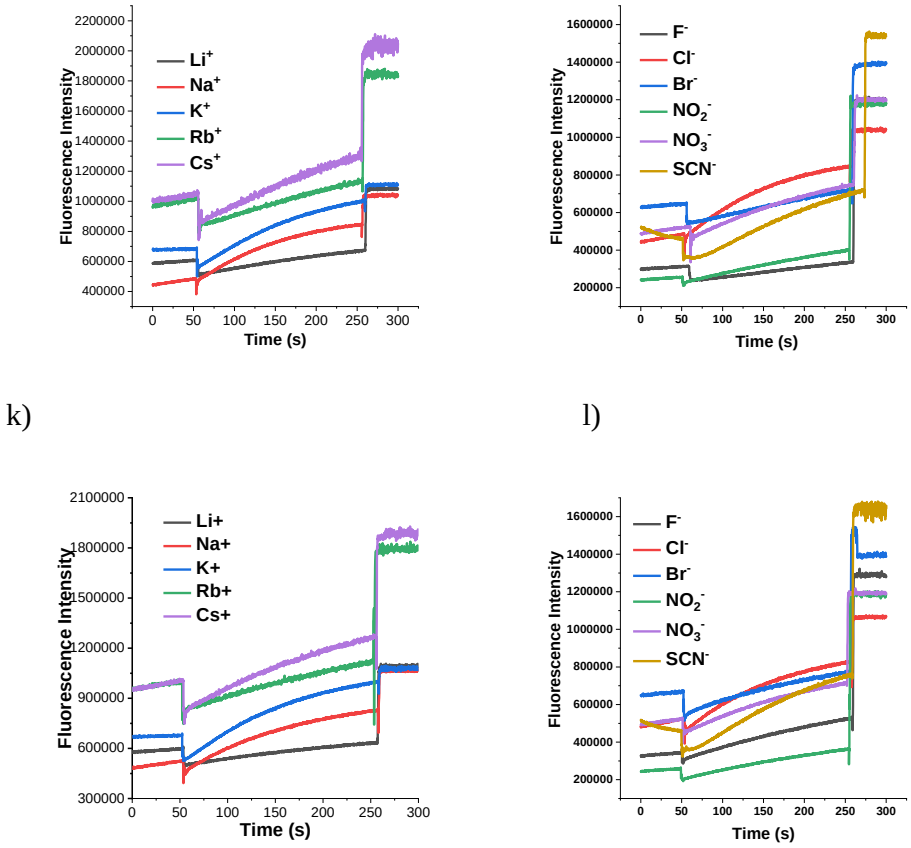


Figure S3. Normalized fluorescence intensity plot of ion transport activity of a) background transport (blank) with varied cation b) background transport (blank) with varied anion c) with DKP **3** when extravesicular cation varied d) with DKP **3** when extravesicular anion varied e) comparison of final intensity of cation transport with respect to blank for DKPs **3** and **5** f) comparison of final intensity of anion transport with respect to blank for DKPs **3** and **5.** (DKP **3/5** = 10.57 µM = 7 mol%) g) raw data of background transport with varied cation h) raw data of background transport with varied anion i) raw data of DKP **3** when extravesicular cation varied j) raw data of DKP **3** when extravesicular anion varied k) raw data of DKP **5** when extravesicular cation varied l) raw data of DKP **5** when extravesicular anion varied

HPTS assay for ion selectivity based on anion/cation gradient (single gradient)

Assay to study cation transport

The vesicle preparation and assay procedure described above was carried out with the 100 mM MCl buffer (10 mM HEPES, 100 mM MCl, (M = Li^+, Na^+, K^+, Cs^+)), only change that pH 7 was used in the extravesicular buffer instead of pH 8 and 7.55 µM (5 mol%) DKP concentration used.

Assay to study anion transport

The assay procedure described above was carried out with the only change that 100 mM NaX (X = F^-, Cl^-, NO_2^-, pH = 7.0) was used in the extravesicular buffer instead of MCl. Background transport of NaX (X = Br^-, NO_3^-, SCN^-) was significant, so these were not considered.

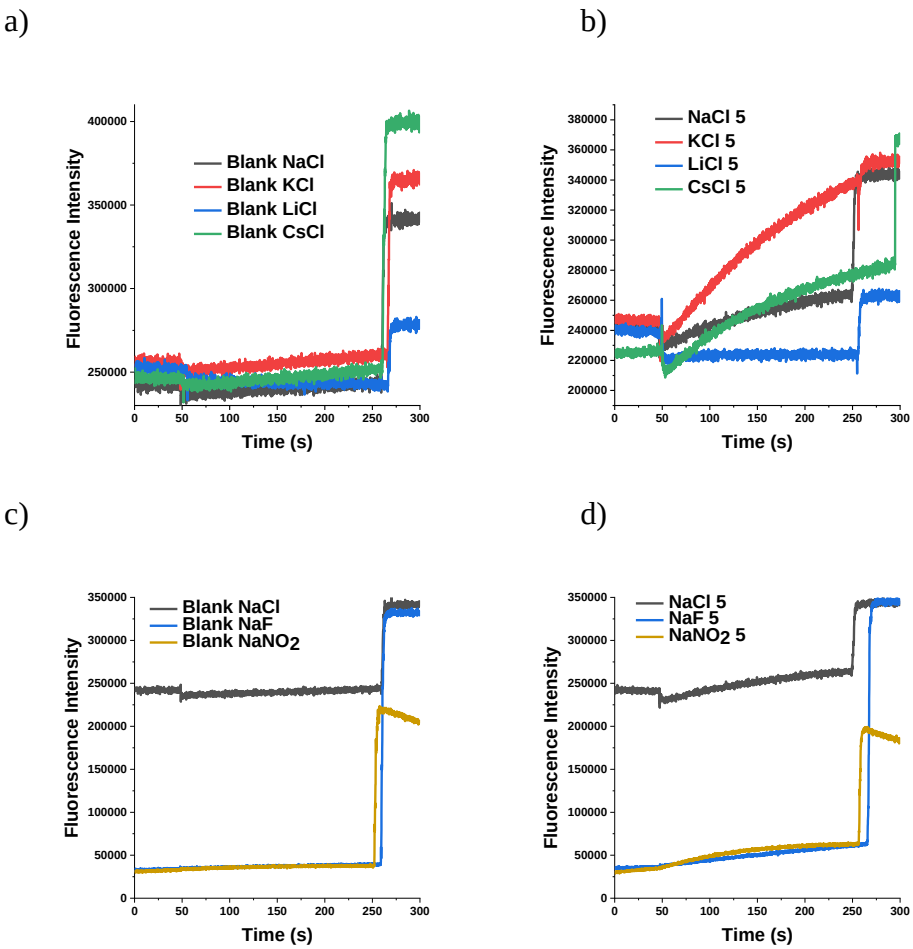


Figure S4. Raw data of a) background transport of various cation in presence of cation gradient b) cation transport activity of DKP **5** in presence of cation gradient c) background transport of various anion in presence of anion gradient d) anion transport activity of DKP **5** in presence of anion gradient

Determination of chloride transport using lucigenin assay

Vesicle preparation

1mL of EYPC lipid in chloroform (25 mg) was taken in a 10 mL round bottom flask. Chloroform was removed using a stream of nitrogen and further kept in vacuo for 3 h at 0 ºC to form a dried lipid film. The lipid film was hydrated by lucigenin dye (1 mL of 1 mM lucigenin, 225 mM $NaNO_3$). The resulting mixture was allowed to stir at room temperature for 1 h and was then subjected to three freeze-thaw cycles. The suspension was extruded 19 times

through 0.2 µm polycarbonate membranes using a mini-extruder obtained from Avanti Polar Lipids. The extra-vesicular dye was removed by size exclusion chromatography using Sephadex G-50 (eluent: 225 mM $NaNO_3$). The milky white vesicle solution was collected and diluted to 3.2 ml to get the 10 mM of lipid stock solution.

Assay to determine cation dependent chloride ion transport activity of 5

30 µL of lucigenin containing vesicle was added to 1970 µL of MCl salt (225 mM, M = Li^+, Na^+, K^+, Cs^+, Rb^+) in a fluorescence cuvette to generate pH gradient across lipid bilayer. This cuvette was placed on the fluorescence instrument equipped with magnetic stirrer. For the fluorescence measurement excitation and emission wavelength used were 455 nm and 505 nm, respectively. A solution of DKP **5** in THF (0.3 mM,10 µL) was added at *t* = 50 s. At *t* = 250 s, Triton-X (20%, 20 µL) was added to lyse the vesicle and achieve the maximum fluorescence quenching. The maximum quenching intensity obtained was used to normalize the fluorescence intensity (Figure 3f).

a) b) c)

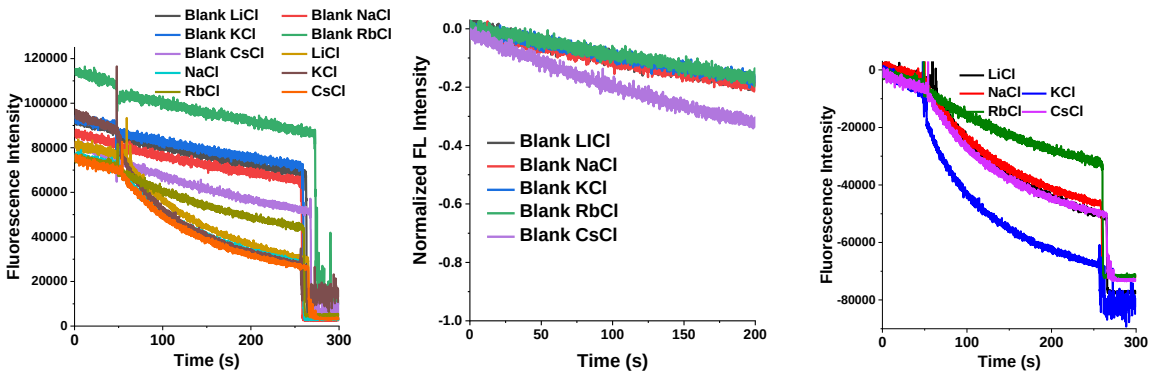


Figure S5. a) Raw data of cation dependent chloride transport activity of DKP **5**; b) Normalized data for (start normalized to 0) background transport with MCl ions; c) data with DKP **5** with start normalized to 0.

Assay to determine comparative chloride ion transport activity of DKP 1-5

The lucigenin assay procedure described above was carried out with the DKP **1-5** (10 µL, 4.53 µM)**.**

a) b)

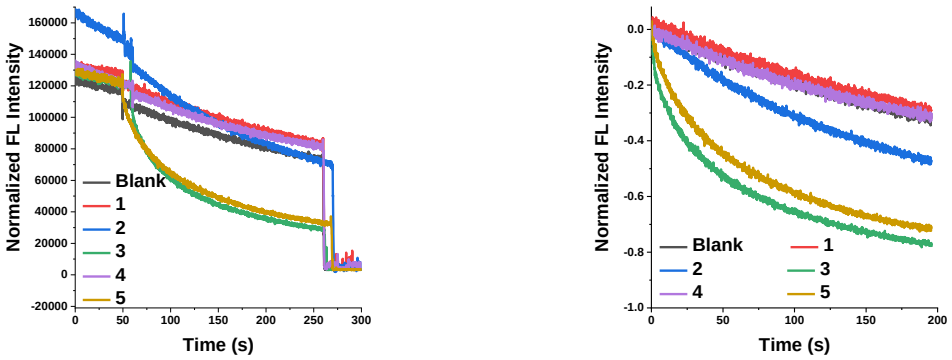


Figure S6. Lucigenin assay a) raw data of comparative chloride transport activity of DKPs **1-5** b) Comparative chloride transport activity of DKPs **1-5**

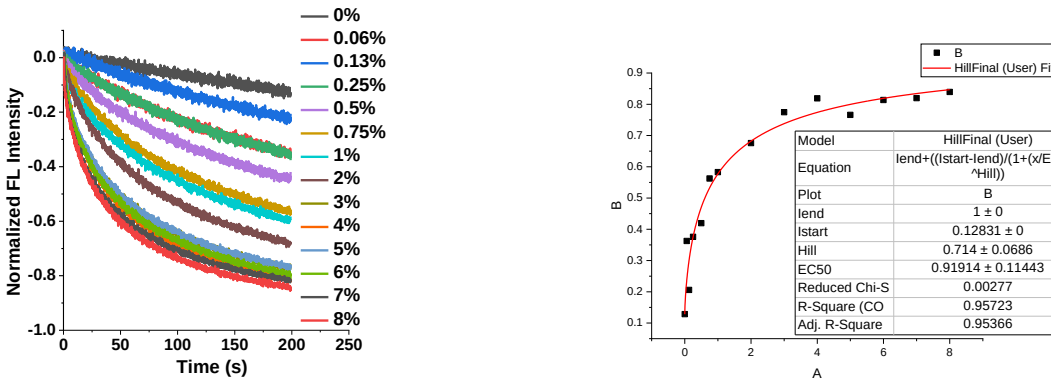
Hill analyses using lucigenin assay

To determine the no. of DKP **3/5** molecules interacting with a single ion in lipid bilayer, concentration dependent lucigenin assay was performed. Vesicle were prepared using earlier discussed procedure of lucigenin assay with extravesicular KCl salt. The concentration of DKP **3/5** was varied from 0 to 12.08 µM in the lucigenin assay. Intensity maxima before addition of Triton-X was plotted against the respective DKP **3/5** concentration to get the Hill plot (Figure S10). Obtained Hill plots were fitted to the Hill equation (Equation S2).

$$I = I_\infty + ((I_0 - I_\infty)/(1+(c/EC_{50})^p)) \quad \text{(S2)}$$

Here, I corresponds to the normalizad intensity, I_∞ and I_0 correspond to the normalized intensity with presence and absence of DKP **3/5**, respectively. The term EC_{50} represents the DKP concentration required to get half of maximum fluorescence intensity. The term p is Hill coefficient and corresponds to number of DKP **3/5** molecule required to transport the single ion.

a) b)



c) d)

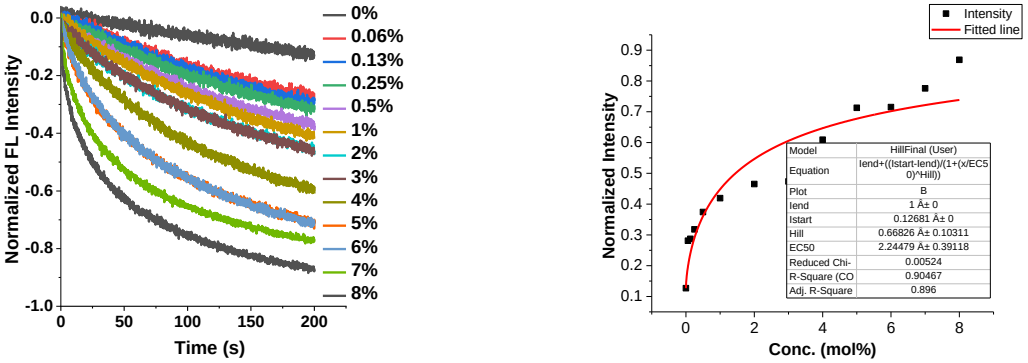


Figure S7. a) Concentration dependent normalized fluorescence intensity of DKP **3** b) Hill plot of DKP **3** c) Concentration dependent normalized fluorescence intensity of DKP **5** d) Hill plot of DKP **5.** The initial and final intensity was kept fixed. The EC_{50} reported in the main paper is the average value of 2 experiments.

HPTS assays for mechanistic studies

Assay in the presence of Gramicidin

Vesicles were prepared as described for the HPTS assay for cation selectivity. The external buffer used was KCl. For the assay a solution of gramicidin (10 µL, 0.122 nM) in DMSO was added at t = 50 s and then solution of DKP **3**/**5** (0.3 mM, 10 µL) in THF was added at t = 100 s. Triton-X (20 µL, 20 %) was added at 300 s to lyse the vesicle and get maximum fluorescence intensity (maximum deprotonated HPTS concentration).

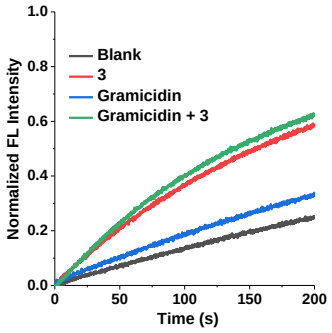


Figure S8. Ion transport activity of DKP **3** in presence of gramicidin

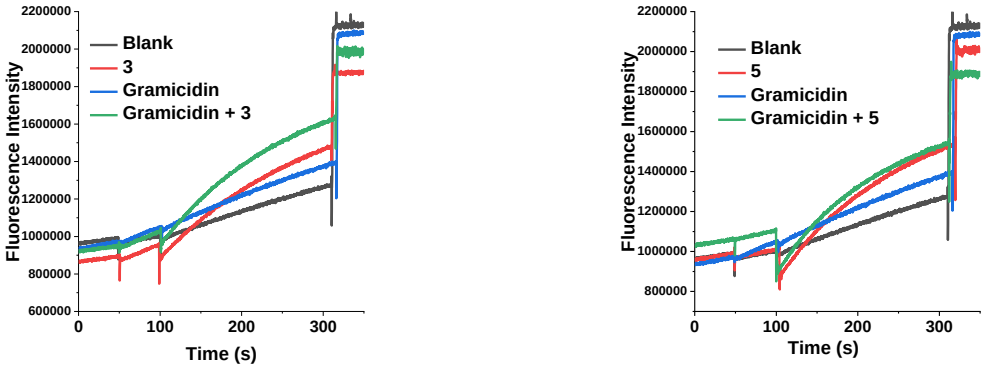


Figure S9. Raw data of ion transport activity of DKP **3/5** in presence of gramicidin

Assay in the presence of Valinomycin

The assay procedure described above for gramicidin was carried out, the only change that addition of valinomycin (10 µL, 1 nM) at t = 50 s instead of gramicidin.

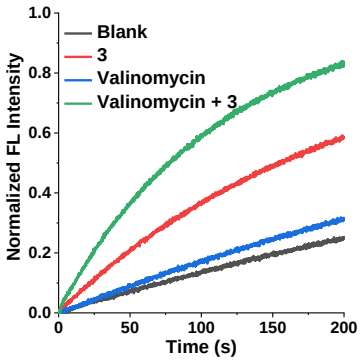


Figure S10. Ion transport activity of DKP **3** in presence of valinomycin

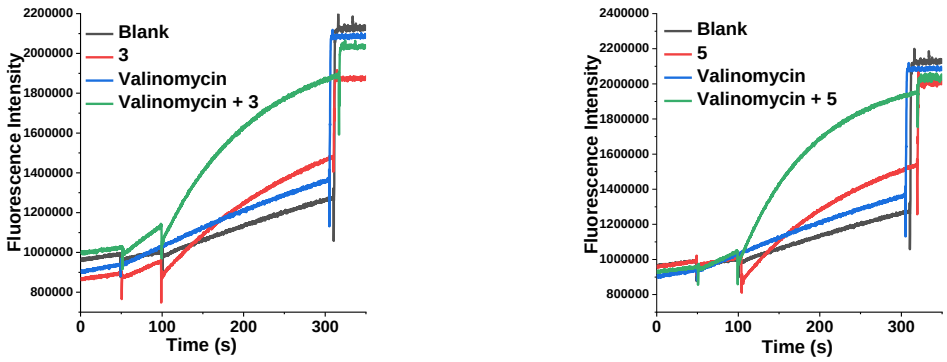


Figure S11. Raw data of ion transport activity of DKP **3/5** in presence of valinomycin

DPPC assay to determine carrier mechanism[3]

10 mL Rb containing 1mL of DPPC lipid in chloroform (25 mg/mL) were dried using stream of nitrogen to produce thin film of lipid. Rb containing thin film of lipid was dried *in vacuo* for 3 hrs. The lipid film was hydrated by lucigenin dye (1 mL of 1 mM, 10 mM sodium phosphate (pH=6.4), 100 mM $NaNO_3$). The resulting mixture was allowed to stir at room temperature for 1 h at 45 ^oC and was then subjected to three freeze-thaw cycles. The suspension was extruded 19 times through 0.2 µm polycarbonate membranes at 45 ^oC using a mini-extruder obtained from Avanti Polar Lipids. The extra-vesicular dye was removed by size exclusion chromatography using Sephadex G-50 (eluent: 10 mM sodium phosphate (pH=6.4), 100 mM $NaNO_3$ buffer). The milky white vesicle solution was collected and diluted to 3.1 mL to get the 11 mM lipid stock solution, assuming 100 % collection of lipid during the size exclusion chromatography.

Assay to study mode of ion transport (channel vs carrier)[3]

100 µL of lucigenin vesicle was added to 1900 µL of sodium phosphate- nitrate (10 mM sodium phosphate, 100 mM $NaNO_3$) buffer and solution of DKP **5** in THF (53.8 µM, 10 mol%) in a fluorescence cuvette. This cuvette was placed in a fluorescence instrument equipped with a magnetic stirrer at 50 ^oC for 2 min to insert the DKP in to vesicle. Further experiment either continue at 50 ^oC or 20 ^oC to check fluidity dependant ion transport activity. For the fluorescence measurement excitation and emission wavelength used were 455 nm and 505 nm, respectively. A aq. solution of NaCl (20 µL, 4 M) was added at t = 50 s. At t = 250 s, Triton-X (20%, 20 µL) was added to lyse the vesicle and achieve the maximum fluorescence quenching. The maximum quenching intensity obtained was used to normalize the fluorescence intensity.

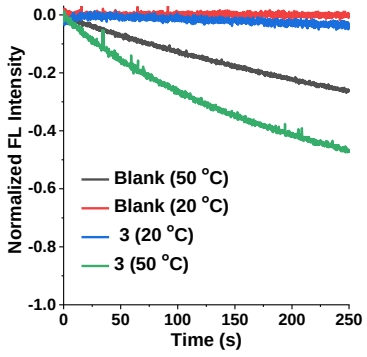


Figure S12. Fluidity dependant ion transport activity of DKP **3**

U-tube experiment to determine carrier mechanism

1 mM (10 mL) of DKP **5** solution in chloroform was added to a U-tube in such a way that the aqueous layers were above the bent of the tube. In this experiment, the organic phase mimics the role of a lipid membrane and separates the two aqueous phases. Aqueous solution of KCl (100 mM, 8 mL) was added to one arm of the tube, which is labelled as source and 8 mL of water was added to the other arm labelled as the receiver arm. 0.5 mL aliquots were collected from the receiver arm at different time intervals and the concentration of Cl^- was measured using chloride electrode and concentration of K^+ was checked using ICP-AES technique.

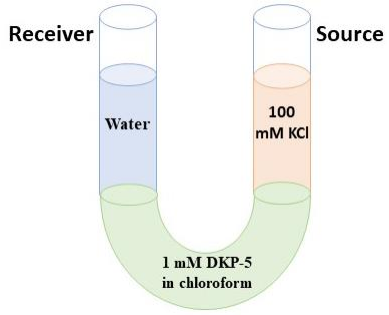


Figure S13. Schematic representation of U-tube experiment

Chloride detection through ion selective electrode

0.5 mL collected aliquots was diluted to 2 mL using deionised water. Ionic strength adjuster (ISA, 40 µL) was added to the resultant mixture under continuous stirring. The chloride concentration was determined using the ISE. Same procedure was repeated for every collected aliquot at time periods as indicated in Table S1.

Potassium detection using ICP-AES technique

0.5 mL collected aliquots at 0, 1, 122, 237 hrs source were diluted to 4 mL (1hrs), 8 mL (122 & 237 hrs) and used for analysis.

Table S1. Concentration of potassium[a] & chloride[b] measured with time

Time (Hrs)	0	1	122	237
Conc. of K^+ in ppm	0	40.2	1065.4	1410.9

Conc of Cl^- in ppm	0	2.4	1720.0	2712.0
Conc. of K^+ in mM	0	1.03	27.25	36.08
Conc. of Cl^- in mM	0	0.07	48.52	76.50
[a]Measured used ICP-AES; [b] measured using a chloride selective electrode				

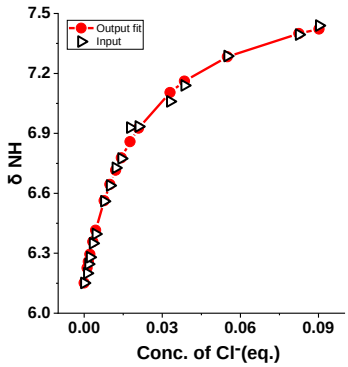
Chloride binding by ^{1}H NMR[4]

NMR binding studies were carried out to probe the chloride binding with norbornene ester DKP **5** (Host) using Cl^- source tetrabutylammonium chloride (TBACl). Concentration of DKP **5** (1 mM, $CDCl_3$) was kept constant throughout the experiment whereas the concentration of TBACl was varied. A solution of TBACl (guest) in chloroform was prepared under nitrogen atmosphere in a glove box. A solution of norbornene ester DKP **5** (200 µL, 2.2 mM) in $CDCl_3$ were added to each NMR tube and the tube was sealed with Teflon tape to avoid solvent evaporation. Increasing amounts of TBACl solution (0 – 254 µL, 166.7 mM in $CDCl_3$) were added to NMR tubes with host solution (200 µL, 2.2 mM). Final volume of all samples was made up to 454 µL by adding the required amount of $CDCl_3$, so that the concentration of host remained constant (1 mM) throughout the experiment.

Table S2. ^{1}H NMR titration data of DKP **5** with TBACl

Sr. No.	Conc. DKP **5** (M)	Conc. Cl^- (M)	Equiv. guest	NH-δ (ppm)	NH-δ fit (ppm)
	0.001	0	0	6.1509	6.1509
	0.001	0.0011	1.1	6.2	6.22615498
	0.001	0.0016	1.6	6.2458	6.25811757
	0.001	0.0022	2.2	6.28	6.29477772
	0.001	0.0033	3.3	6.35	6.35757729
	0.001	0.0044	4.4	6.3963	6.41524095
	0.001	0.0077	7.7	6.56	6.56287985
	0.001	0.0099	9.9	6.6386	6.64440746
	0.001	0.0121	12.1	6.7276	6.71539656
	0.001	0.0143	14.3	6.7743	6.77773307
	0.001	0.0176	17.6	6.929	6.85813871
	0.001	0.0209	20.9	6.934	6.92603541

	0.001	0.033	33	7.06	7.10440062
	0.001	0.0385	38.5	7.14	7.16154102
	0.001	0.055	55	7.2867	7.28326703
	0.001	0.0825	82.5	7.3938	7.39964479
	0.001	0.0902	90.2	7.4396	7.42187206



http://app.supramolecular.org/bindfit/view/09478069-e316-486a-86ff-ebd13f215d74

Figure S14. ^{1}H NMR plot

Evidence of KCl binding by Mass Spectrometry

Electrospray ionization mass spectrometric (ESI-MS) studies were carried out to obtain direct evidence of anion recognition by DKP **5**. Samples were prepared in THF:Water:Methanol (9:1:1) by mixing DKP **5** with KCl in 1:3 molar ratios and then electrosprayed with flow rate 0.2 mL/min, capillary voltage 3000 v and nozzle voltage 5 v. The (ESI-MS spectra revealed the formation of DKP KCl− adduct detected at m/z= 511.1007.

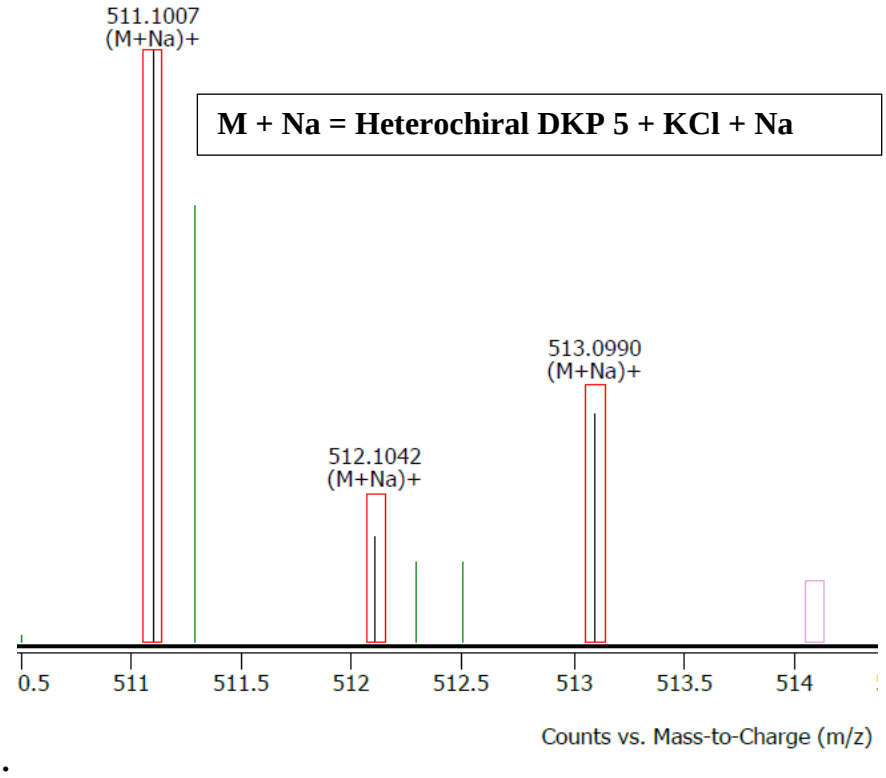
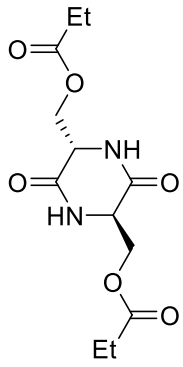


Figure S15. Mass spectrum of heterochiral DKP **5**.KCl

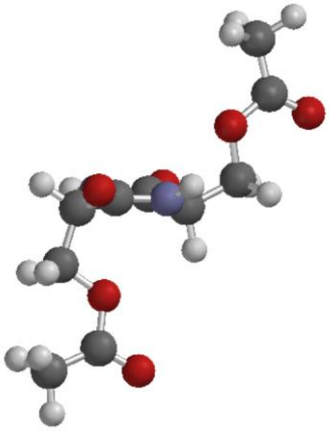
Computational studies with a model DKP diester

Geometry optimization for model peptide **7 (**Figure S16a) was done using PC SPARTAN PRO program. Geometry optimization was first done using molecular mechanics (MMFF), following which semi-empirical (AM1) and Hartree-Foc (STO-3G) models were used (Figure S16b). The energy minimum was confirmed by ensuring the absence of imaginary frequencies. The x, y, z coordinates are given in Table S3 and the list of vibrational frequencies (first 50 lines) is given in Table S4. The optimized structure matched the crystal structure obtained for DKP **5**.[1] The structure of the chloride bound DKP **7** was also computed using a similar level of theory (Figure S16a). The x, y, z coordinates are given in Table S5 and the list of vibrational frequencies (first 50 lines) is given in Table S6.

a) b) c)



7



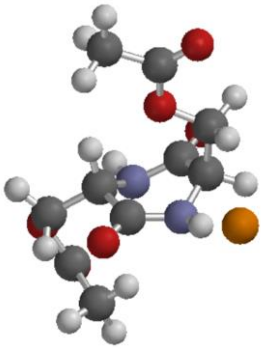


Figure S16. a) Model diketopiperazine **7**. b) Optimized geometry of DKP **7**; c) Optimized geometry of DKP**7**.Cl

Table S3. x, y, z, co-ordinates for DKP **7**.

Number	Label	x	y	z
1	N	-0.313	1.093	-0.709
2	H	-0.884	1.546	-1.387
3	C	0.52	1.849	0.076
4	O	0.749	3.047	-0.177
5	C	1.211	1.173	1.277
6	H	1.322	1.974	2.073
7	N	0.437	0.103	1.838
8	H	0.71	-0.238	2.731
9	C	-0.38	-0.692	1.053
10	O	-0.904	-1.713	1.53
11	C	-0.603	-0.289	-0.417
12	H	0.135	-0.93	-1.003
13	C	2.65	0.8	0.85
14	H	3.145	1.711	0.421
15	C	-2.01	-0.727	-0.862
16	H	-2.193	-1.786	-0.537
17	H	-2.126	-0.639	-1.973
18	O	-2.962	0.143	-0.236
19	C	-4.279	-0.233	-0.314
20	O	-4.558	-1.229	-0.982
21	C	-5.181	0.67	0.45
22	H	-5.256	0.295	1.501
23	H	-6.195	0.662	-0.019
24	H	3.234	0.419	1.728
25	O	2.555	-0.224	-0.138
26	C	3.725	-0.632	-0.744

27	O	3.521	-1.516	-1.574
28	C	5.026	-0.015	-0.373
29	H	5.212	-0.135	0.722
30	H	5.021	1.074	-0.625
31	H	5.85	-0.515	-0.94
32	H	-4.778	1.711	0.465

Table S4. List of vibrational frequencies obtained for DKP **7**

S.No	Frequency	Type
1	20.44	A
2	30.40	A
3	40.78	A
4	47.68	A
5	51.22	A
6	60.94	A
7	85.90	A
8	120.69	A
9	129.49	A
10	149.46	A
11	169.55	A
12	176.01	A
13	185.80	A
14	222.92	A
15	266.13	A
16	312.08	A
17	325.06	A
18	401.83	A
19	412.77	A
20	442.45	A
21	453.24	A
22	482.90	A
23	488.86	A
24	542.76	A
25	554.64	A
26	557.27	A
27	565.88	A
28	570.69	A
29	586.92	A
30	615.90	A
31	678.98	A
32	763.85	A
33	791.54	A
34	848.28	A
35	896.95	A
36	938.08	A

37	1012.09	A
38	1034.87	A
39	1044.31	A
40	1050.27	A
41	1069.14	A
42	1070.57	A
43	1072.52	A
44	1110.34	A
45	1131.84	A
46	1136.50	A
47	1214.26	A
48	1226.90	A
49	1231.23	A
50	1240.81	A

Table S5. x, y, z coordinates of DKP **7**.Cl

Number	Label	x	y	z
1	N	0.183	0.145	-1.729
2	C	0.513	0.962	-0.628
3	O	0.787	2.152	-0.71
4	C	0.652	0.221	0.748
5	H	-0.297	0.34	1.279
6	N	0.953	-1.213	0.526
7	H	1.078	-1.707	1.42
8	C	-0.005	-1.917	-0.291
9	O	-0.282	-3.085	-0.075
10	C	-0.58	-1.087	-1.472
11	H	-0.494	-1.709	-2.368
12	C	1.782	0.888	1.608
13	H	2.218	1.712	1.037
14	C	-2.108	-0.84	-1.286
15	H	-2.641	-1.797	-1.275
16	H	-2.45	-0.242	-2.142
17	O	-2.315	-0.136	-0.044
18	C	-3.647	0.181	0.181
19	O	-4.567	-0.2	-0.517
20	C	-3.782	1.053	1.445
21	H	-3.398	0.518	2.308
22	H	-4.825	1.302	1.61
23	H	1.338	1.32	2.509
24	O	2.772	-0.029	2.094
25	C	3.709	-0.516	1.169
26	O	4.378	-1.47	1.521
27	C	3.907	0.196	-0.187
28	H	4.135	1.248	-0.046
29	H	3.022	0.106	-0.81

30	H	4.74	-0.281	-0.691
31	H	-3.208	1.967	1.323
32	H	-0.257	0.66	-2.575
33	Cl	-1.312	1.257	-3.933

Table S6. List of vibrational frequencies obtained for DKP **7**.Cl

S.No	Frequency	Type
1	19.92	A
2	27.44	A
3	37.54	A
4	42.80	A
5	45.48	A
6	47.25	A
7	67.87	A
8	78.55	A
9	84.71	A
10	106.87	A
11	129.65	A
12	155.12	A
13	176.42	A
14	191.11	A
15	214.36	A
16	226.96	A
17	248.00	A
18	300.52	A
19	334.72	A
20	358.61	A
21	415.18	A
22	450.41	A
23	468.57	A
24	494.58	A
25	506.11	A
26	527.89	A
27	587.73	A
28	603.21	A
29	607.88	A
30	642.61	A
31	675.02	A
32	693.56	A
33	731.58	A
34	760.47	A
35	829.01	A
36	880.98	A
37	912.40	A
38	929.91	A

39	971.19	A
40	1052.55	A
41	1099.12	A
42	1130.77	A
43	1164.30	A
44	1180.06	A
45	1203.76	A
46	1214.04	A
47	1221.21	A
48	1260.93	A
49	1327.44	A
50	1334.65	A

The minimized structure of **7** was used to optimize the structure of the bound KCl.DKP complex (Figure S17) using the same level of theory. The energy minimum was confirmed by ensuring the absence of imaginary frequencies. The x, y, z coordinates are given in Table S7 and the list of vibrational frequencies (first 50 lines) is given in Table S8.

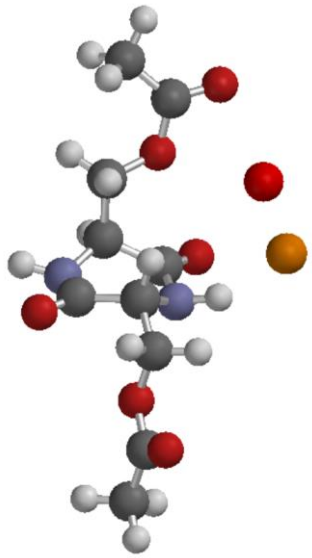


Figure S17. Optimized geometry of DKP**7**.KCl complex. Chloride in Orange and Potassium in Red.

Table S7. x, y, z, co-ordinates for DKP **7**.KCl

Number	Label	x	y	z
1	N	0.933	0.239	0.766
2	C	0.347	1.497	0.547
3	O	0.467	2.438	1.337
4	C	-0.461	1.681	-0.772
5	H	-0.361	2.725	-1.076
6	N	0.106	0.831	-1.821

7	C	0.306	-0.563	-1.548
8	O	0.348	-1.385	-2.446
9	C	0.474	-0.912	-0.041
10	H	-0.496	-1.278	0.323
11	C	-1.982	1.405	-0.487
12	H	-2.589	1.833	-1.291
13	C	1.48	-2.082	0.118
14	H	1.09	-2.965	-0.402
15	H	1.579	-2.327	1.181
16	O	2.735	-1.663	-0.445
17	C	3.714	-2.651	-0.35
18	O	3.507	-3.749	0.127
19	C	5.044	-2.141	-0.93
20	H	4.908	-1.854	-1.969
21	H	5.795	-2.922	-0.866
22	H	-2.169	0.326	-0.451
23	O	-2.302	2.009	0.781
24	C	-3.604	1.893	1.268
25	O	-3.729	2.122	2.462
26	C	-4.766	1.554	0.32
27	H	-4.821	2.282	-0.485
28	H	-5.688	1.578	0.891
29	H	5.378	-1.271	-0.373
30	H	-0.262	1.007	-2.761
31	K	-1.226	2.121	3.175
32	H	-4.635	0.563	-0.106
33	Cl	-0.027	-0.343	3.533
34	H	0.908	0.004	1.79

Table S8. List of vibrational frequencies obtained for DKP **7.**KCl Complex

S.No	Frequency	Type
1	22.53	A
2	25.75	A
3	31.86	A
4	40.56	A
5	51.23	A
6	67.95	A
7	82.47	A
8	92.16	A
9	99.12	A
10	113.85	A
11	134.28	A
12	143.24	A
13	156.94	A
14	178.96	A
15	190.65	A

16	210.22	A
17	220.04	A
18	230.67	A
19	259.82	A
20	298.72	A
21	309.61	A
22	322.39	A
23	369.95	A
24	393.84	A
25	414.12	A
26	447.56	A
27	453.84	A
28	492.96	A
29	552.47	A
30	577.04	A
31	605.94	A
32	617.06	A
33	620.30	A
34	630.43	A
35	665.14	A
36	694.33	A
37	757.87	A
38	797.42	A
39	849.11	A
40	883.64	A
41	926.00	A
42	962.10	A
43	1038.70	A
44	1060.30	A
45	1131.92	A
46	1151.42	A
47	1176.99	A
48	1190.85	A
49	1226.11	A
50	1226.43	A

Spectra of compounds

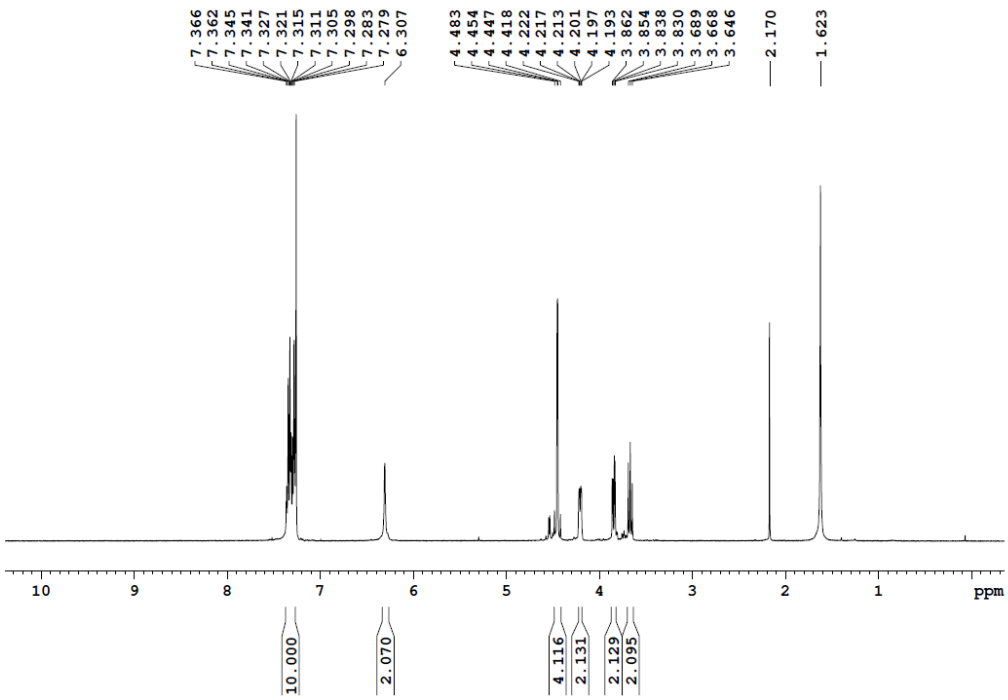


Figure S18. ^{1}H NMR spectrum of DKP-**2**

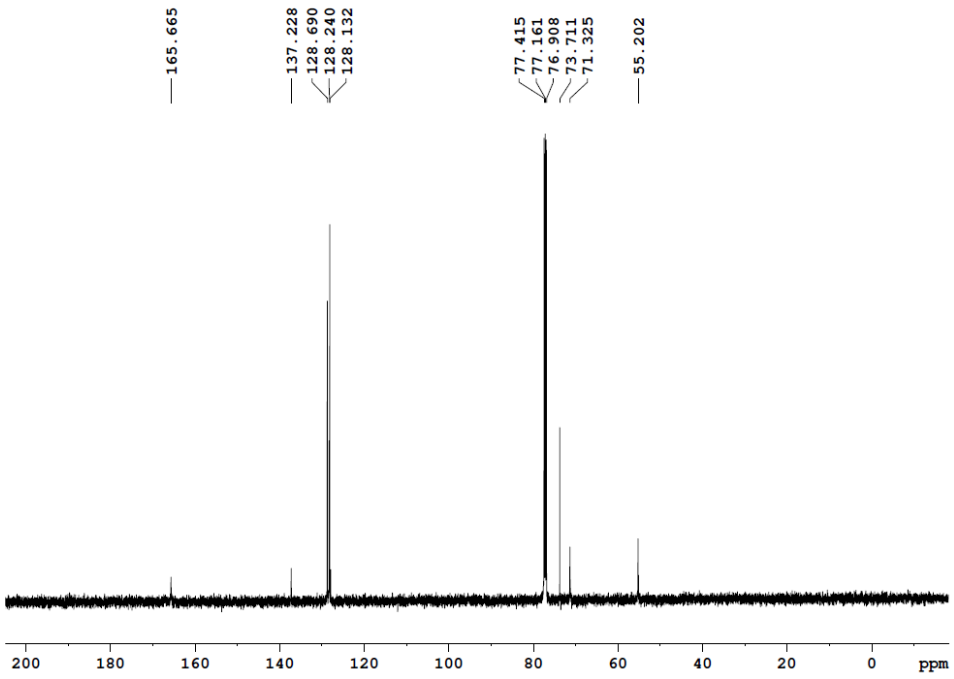


Figure S19. ^{13}C NMR spectrum of DKP-**2**

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