

Supporting Information

Study on translational diffusion of solute molecules in novel phosphonium-based dicationic ionic liquids by transient grating spectroscopy

Masaki Fujiwara,^{†a} Shinya Okazoe,^{†a} Sawaya Suzuki,^a Koji Osawa,^b Takatsugu Endo,^b and Yoshifumi Kimura^{*a}

^a*Graduate School of Science and Eengineering, Doshisha University, Kyotanabe-City, Kyoto 610-0321, Japan.*

^b*Faculty of Science and Engineering, Doshisha University, Kyotanabe-City, Kyoto 610-0321, Japan.*

†: Co-first Author.

*: Corresponding Author.

Table S1. Viscosity of [C_nmim][NTf₂] (n = 5 and 10) at various temperatures.

ILs	<i>T</i> / <i>K</i>	<i>η</i> / <i>mPa s</i>
[C ₅ mim][NTf ₂]	298.3	62.2
	303.2	49.0
	307.4	40.2
	312.1	33.6
	316.5	28.4
	323.2	22.4
	328.2	19.2
	333.2	16.5
	338.2	14.4
	343.2	12.7
	348.2	11.2
	353.2	10.2
	358.2	8.9
	363.2	8.0
	368.2	7.3
373.2	6.6	
[C ₁₀ mim][NTf ₂]	298.4	114.5
	303.2	88.3
	307.8	69.3
	312.3	55.5
	316.5	45.5
	321.5	36.8
	326.9	31.2
	331.7	26.6
	336.7	22.7
	341.5	19.7
	346.4	17.3
	351.3	15.1
	356.2	13.5
	361.1	12.0
	365.9	10.9
370.8	9.8	

Table S2. Viscosity of $[\text{C}_{10}(\text{mim})_2][\text{NTf}_2]_2$ at various temperatures.

ILs	T / K	$\eta / \text{mPa s}$
$[\text{C}_{10}(\text{mim})_2][\text{NTf}_2]_2$	298.4	679.4
	303.2	491.4
	307.8	356.8
	312.3	276.5
	316.5	204.4
	321.5	164.0
	326.9	124.9
	331.7	101.1
	336.7	83.2
	341.5	69.3
	346.4	58.2
	351.3	49.5
	356.2	42.4
	361.1	37.0
	365.9	32.2
370.8	28.2	

Table S3. Viscosity of $[(P_{888})_2C_n][NTf_2]_2$ ($n = 6$ and 10) at various temperatures.

ILs	T / K	$\eta / mPa s$
$[(P_{888})_2C_6][NTf_2]_2$	322.8	511.2
	332.4	308.4
	341.9	197.7
	351.4	132.6
	361.0	91.80
	370.5	65.20
	380.0	47.89
$[(P_{888})_2C_{10}][NTf_2]_2$	322.8	431.7
	332.4	265.8
	341.9	172.1
	351.4	116.6
	361.0	81.72
	370.5	59.19
	380.0	43.69

Table S4. VFT parameters (Eq. (4)) of various ILs.

ILs	$\ln \eta_0$	B / K	T_0 / K
$[C_5mim][NTf_2]$	-1.48 ± 0.11	637 ± 31	185 ± 4
$[C_{10}mim][NTf_2]$	-0.926 ± 0.107	539 ± 27	203 ± 3
$[C_{10}(mim)_2][NTf_2]_2$	-0.929 ± 0.087	725 ± 22	201 ± 2
$[(P_{888})_2C_6][NTf_2]_2$	-3.29 ± 0.21	1649 ± 84	150 ± 5
$[(P_{888})_2C_{10}][NTf_2]_2$	-3.00 ± 0.12	1537 ± 49	153 ± 3

Table S5. Diffusion coefficients of CO, DPA, and DPCP at various temperatures in imidazolium-based ILs used in this study.

ILs	T/K	$D_{CO}/10^{-10}m^2s^{-1}$	$D_{DPA}/10^{-11}m^2s^{-1}$	$D_{DPCP}/10^{-11}m^2s^{-1}$
[C ₅ mim][NTf ₂]	311.5	6.64±0.11	6.00±0.11	3.63±0.04
	322.4	8.22±0.15	9.09±0.18	5.41±0.05
	331.3	10.5±0.2	11.7±0.3	7.33±0.05
	340.4	12.7±0.2	14.9±0.4	9.50±0.13
	349.7	15.8±0.3	18.8±0.5	12.3±0.2
[C ₁₀ mim][NTf ₂]	311.5	5.21±0.09	6.02±0.01	2.46±0.06
	322.4	8.40±0.11	8.10±0.28	4.02±0.08
	331.3	10.4±0.3	10.9±0.2	5.63±0.12
	340.4	13.1±0.4	13.8±0.4	7.74±0.21
	349.7	15.9±0.4	17.7±0.6	10.3±0.3
[C ₁₀ (mim) ₂][NTf ₂] ₂	311.5	1.69±0.03	1.00±0.00	0.378±0.002
	322.4	2.40±0.03	1.79±0.02	0.719±0.006
	331.3	3.31±0.07	2.68±0.06	1.16±0.02
	340.4	4.44±0.06	3.82±0.11	1.77±0.03
	349.7	5.86±0.20	5.24±0.14	2.63±0.03

Table S6. Diffusion coefficients of thermal, CO, DPA, and DPCP in phosphonium-based ILs used in this study.

ILs	T/K	$D_{co}/10^{-10}m^2s^{-1}$	$D_{DPA}/10^{-11}m^2s^{-1}$	$D_{DPCP}/10^{-11}m^2s^{-1}$	$D_{th}/10^{-8}m^2s^{-1}$
[(P ₈₈₈) ₂ C ₆][NTf ₂] ₂	331.3	8.44±0.12	3.33±0.04	1.43±0.02	7.52±0.06
	340.4	10.1±0.0	4.80±0.11	2.07±0.03	7.33±0.03
	349.7	12.6±0.2	6.75±0.21	3.05±0.03	7.33±0.06
	357.7	14.8±0.2	8.34±0.18	4.11±0.04	7.23±0.05
	366.4	17.2±0.3	10.9±0.2	5.48±0.03	7.16±0.08
[(P ₈₈₈) ₂ C ₁₀][NTf ₂] ₂	331.3	7.54±0.05	3.69±0.04	1.48±0.01	7.60±0.03
	340.4	9.11±0.13	5.28±0.08	2.11±0.04	7.48±0.03
	349.7	11.8±0.0	6.84±0.12	3.21±0.03	7.40±0.04
	357.7	14.2±0.2	9.01±0.14	4.31±0.02	7.30±0.04
	366.4	17.3±0.2	10.5±0.2	5.78±0.03	7.27±0.03

Table S7. Fitting parameters of Eq. (7) for D_{CO} .

ILs	$D_0 / 10^{-10}$	α
[C ₅ mim][NTf ₂]	1.41	0.686
[C ₁₀ mim][NTf ₂]	1.50	0.766
[C ₁₀ (mim) ₂][NTf ₂] ₂	1.52	0.690
[(P ₈₈₈) ₂ C ₆][NTf ₂] ₂	8.31	0.459
[(P ₈₈₈) ₂ C ₁₀][NTf ₂] ₂	6.71	0.552
[P ₄₄₄₁][NTf ₂] ^{a)}	2.47	0.671
[P ₈₈₈₈][NTf ₂] ^{a)}	6.44	0.509

a) taken from ref. [1].

Table S8. Fitting parameters of Eq. (7) for D_{DPA} .

ILs	$D_0 / 10^{-11}$	α
[C ₅ mim][NTf ₂]	0.856	0.888
[C ₁₀ mim][NTf ₂]	1.63	0.757
[C ₁₀ (mim) ₂][NTf ₂] ₂	0.926	0.912
[(P ₈₈₈) ₂ C ₆][NTf ₂] ₂	3.35	0.749
[(P ₈₈₈) ₂ C ₁₀][NTf ₂] ₂	3.37	0.696
[P ₄₄₄₁][NTf ₂] ^{a)}	1.55	0.818
[P ₈₈₈₈][NTf ₂] ^{a)}	2.01	0.867

a) taken from ref. [1].

Table S9. Fitting parameters of Eq. (7) for D_{DPCP} .

ILs	$D_0 / 10^{-12}$	α
[C ₅ mim][NTf ₂]	4.33	0.961
[C ₁₀ mim][NTf ₂]	4.57	1.00
[C ₁₀ (mim) ₂][NTf ₂] ₂	3.38	1.07
[(P ₈₈₈) ₂ C ₆][NTf ₂] ₂	14.0	0.863
[(P ₈₈₈) ₂ C ₁₀][NTf ₂] ₂	12.5	0.907
[P ₄₄₄₁][NTf ₂] ^{a)}	6.50	0.895
[P ₈₈₈₈][NTf ₂] ^{a)}	6.82	1.00

a) taken from ref. [1].

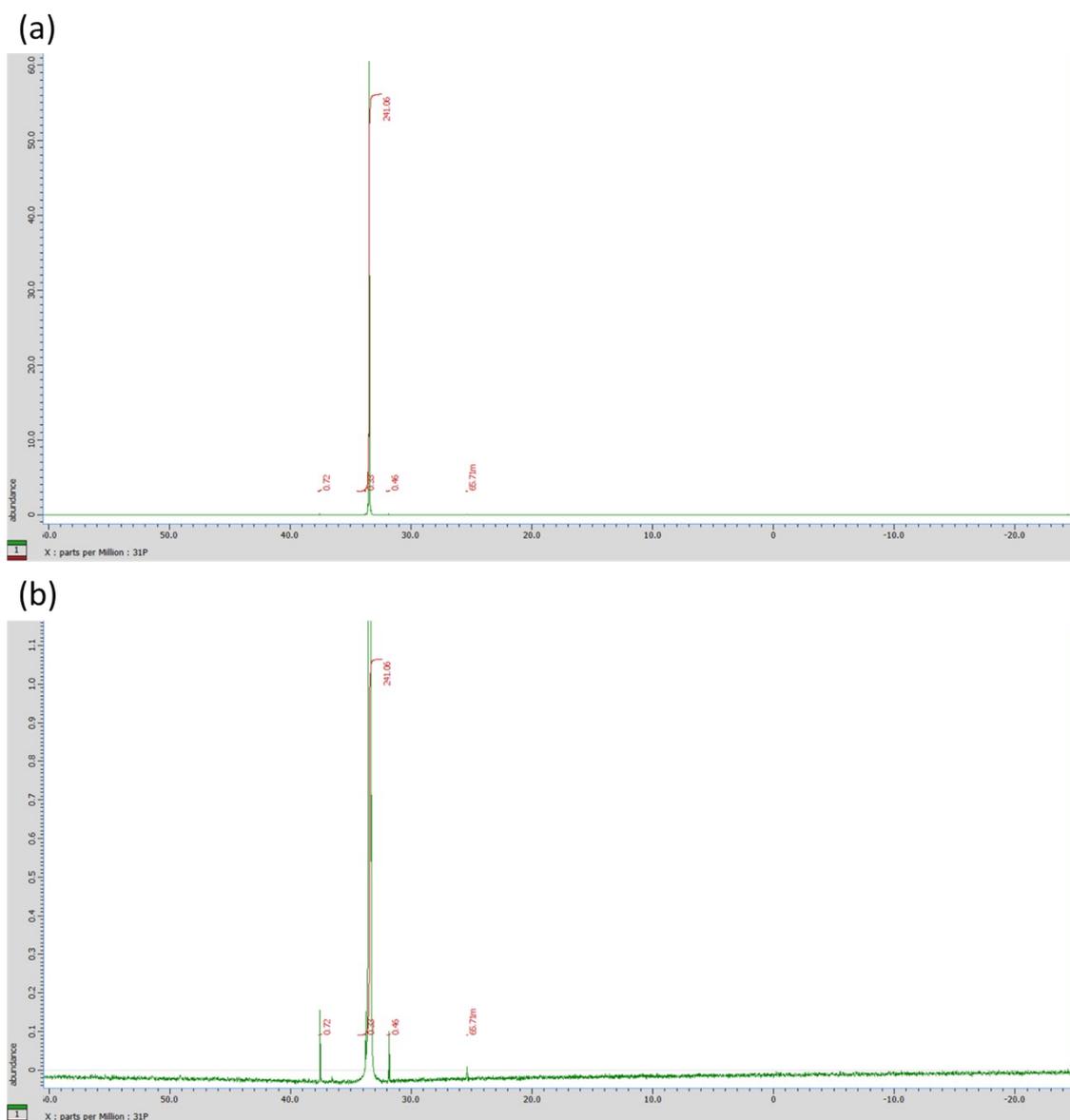


Fig. S1. (a) Whole and (b) magnification of the low intensity region of ^{31}P NMR spectra of $[(\text{P}_{888})_2\text{C}_6][\text{NTf}_2]_2$.

The strongest peak at 33.47 ppm is assigned to phosphonium. The integral value of this peak was calculated to be 240.73 by subtracting the shoulder peak at 33.78 ppm (integral value: 0.33).

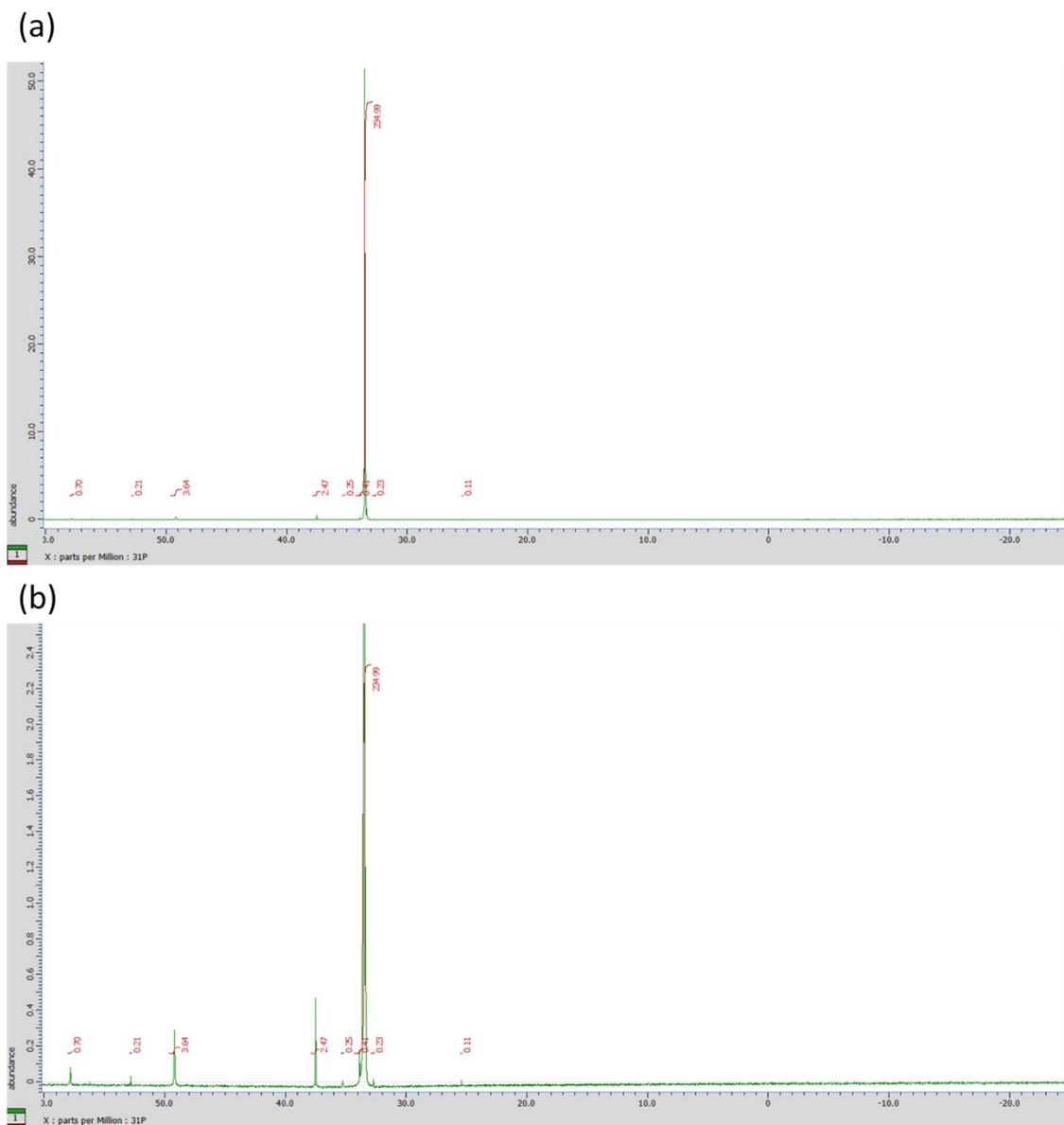


Fig. S2. (a) Whole and (b) magnification of the low intensity region of ^{31}P NMR spectra of $[(\text{P}_{888})_2\text{C}_{10}][\text{NTf}_2]_2$.

The strongest peak at 33.51 ppm is assigned to phosphonium. The integral value of this peak was calculated to be 234.58 by subtracting the shoulder peak at 33.87 ppm (integral value: 0.41).

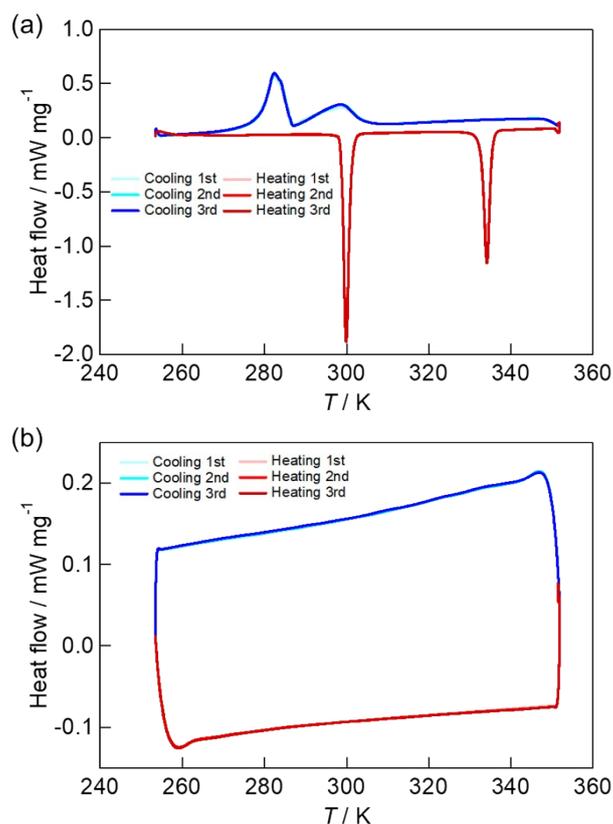


Fig. S3. DSC profiles of (a) [(P₈₈₈)₂C₆][BF₄]₂ and (b) [(P₈₈₈)₂C₁₀][BF₄]₂ scanned at 5 K min⁻¹.

[(P₈₈₈)₂C₆][BF₄]₂ and [(P₈₈₈)₂C₁₀][BF₄]₂ were solid at room temperature. Also, they were liquid during evacuation in the oil bath whose temperature was set to 333K. To estimate melting point or glass transition temperature, we performed DSC measurements. The temperature was varied from 353 K to 253 K. As shown in Fig. S3(a), [(P₈₈₈)₂C₆][BF₄]₂ showed two phase transition at around 300 K and 334 K. The latter phase transition was assigned to melting, and the former was solid-solid phase transition. On the other hand, no clear phase transition was detected for [(P₈₈₈)₂C₁₀][BF₄]₂ (Fig. S3(b)). It might have glass transition point between 293 K (room temperature) and 333 K considering the apparent states through the experiments.

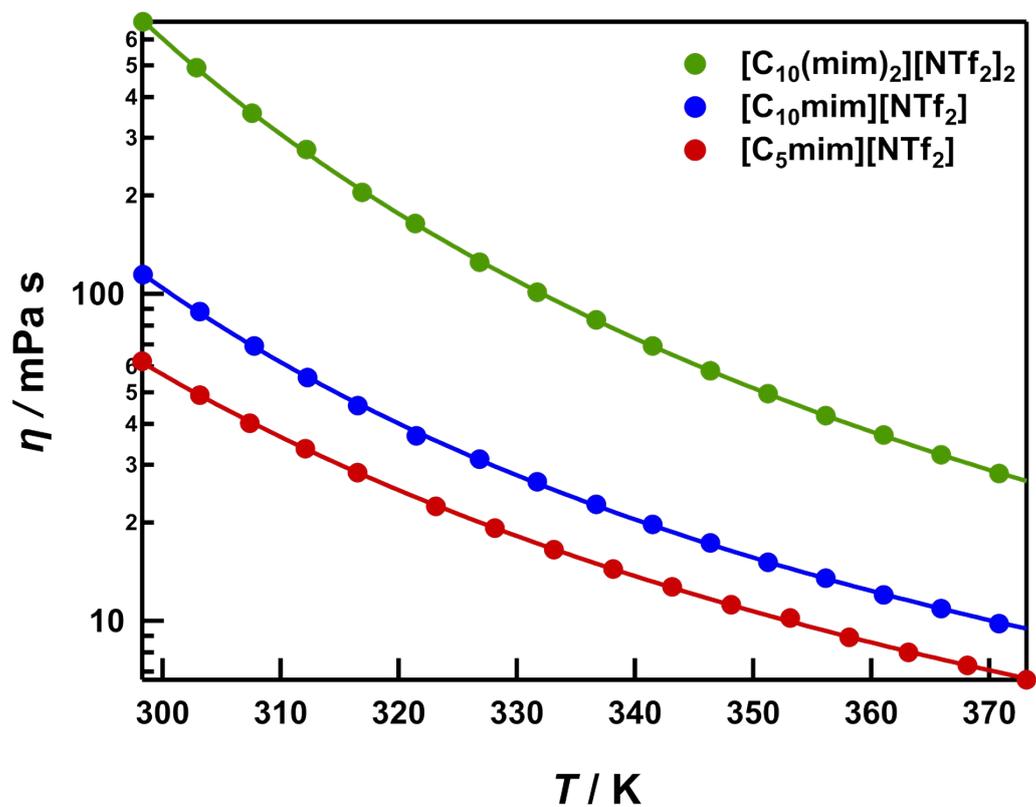


Fig. S4. Viscosity of $[C_nmim][NTf_2]$ ($n = 5$ and 10) and $[C_{10}(mim)_2][NTf_2]_2$ as function of temperature. The vertical axis is logarithmic in scale. The solid lines represent the fitting curves by Eq. (4).

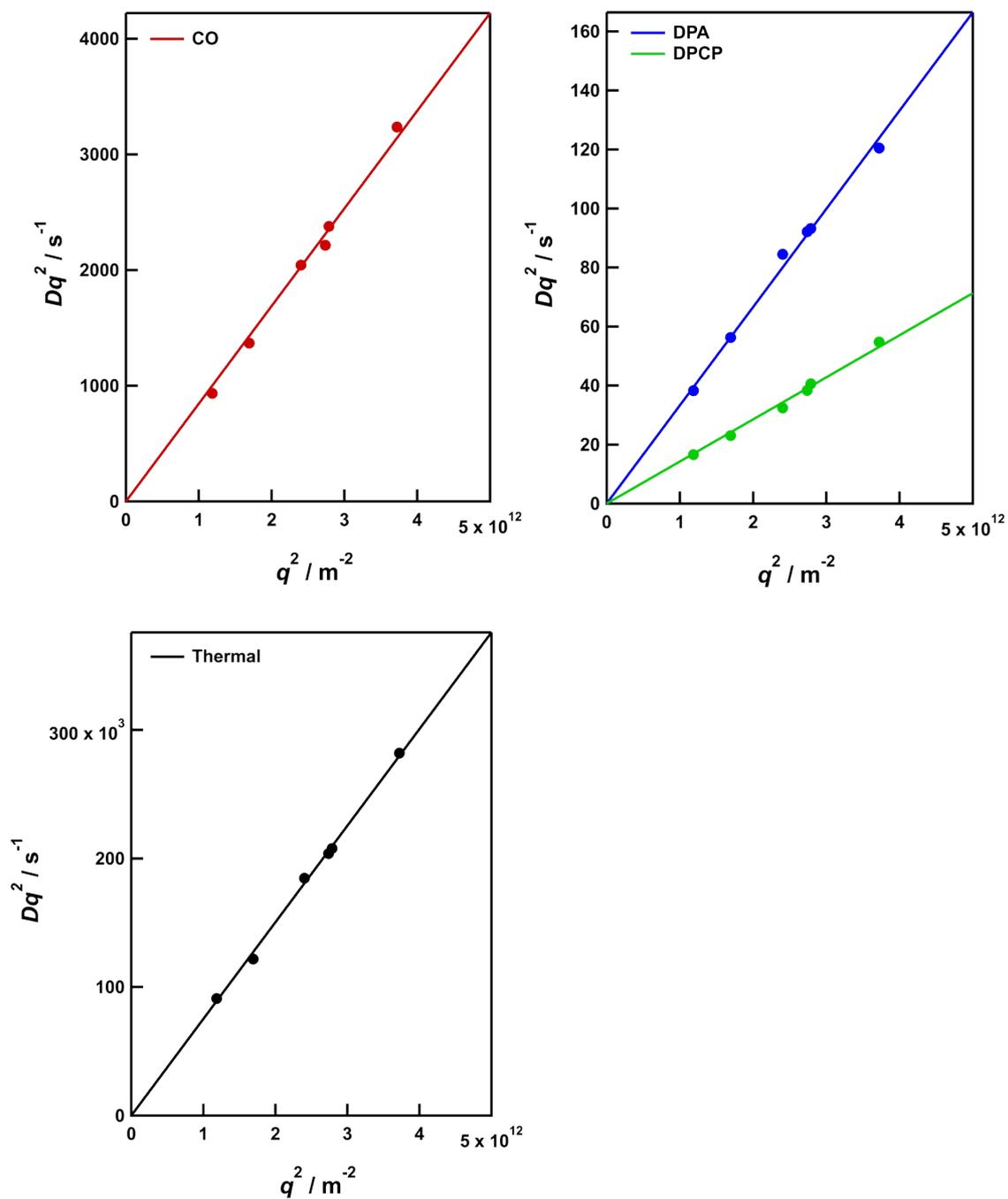


Fig. S5. Plot of decay rates Dq^2 of CO, DPA, DPCP and thermal gratings against q^2 in $[(\text{P}_{888})_2\text{C}_6][\text{NTf}_2]_2$ at 331 K.

References

- [1] Y. Kimura *et al.*, *J. Phys. Chem. B*, 2015, **119**, 8096-8103.