

Supporting Information:

Table S1: Ion Size Dependence of TICT molecules in 0.5(M) Perchlorate Solutions of Acetonitrile ^{a)}

(A) Spectral properties and area ratio: P4C

| Ion | $\frac{z}{r_{ion}}$ | ν_{abs} | Γ_{abs} | ν_{LE} | Γ_{LE}^{inh} | ν_{CT} | Γ_{CT}^{inh} | $\frac{\alpha_{CT}}{\alpha_{LE}}$ |
|------------------|---------------------|-------------|----------------|------------|---------------------|------------|---------------------|-----------------------------------|
| Na ⁺ | 0.980 | 34.30 | 4.22 | 27.33 | 1.39 | 19.38 | 3.61 | 0.93 |
| Li ⁺ | 1.351 | 34.67 | 4.19 | 27.40 | 1.40 | 19.15 | 3.70 | 0.86 |
| Sr ⁺² | 1.724 | 34.11 | 4.39 | 27.15 | 1.12 | 18.87 | 3.16 | 1.31 |
| Ca ⁺² | 2.000 | 34.16 | 4.43 | 27.31 | 1.39 | 18.52 | 3.81 | 1.18 |
| Mg ⁺² | 2.780 | 33.96 | 4.71 | 27.23 | 1.12 | 19.33 | 3.04 | 0.82 |

(B) Spectral properties and area ratio: P5C

| Ion | ν_{abs} | Γ_{abs} | ν_{LE} | Γ_{LE}^{inh} | ν_{CT} | Γ_{CT}^{inh} | $\frac{\alpha_{CT}}{\alpha_{LE}}$ |
|------------------|-------------|----------------|------------|---------------------|------------|---------------------|-----------------------------------|
| Na ⁺ | 33.74 | 4.13 | 27.54 | 1.65 | 19.37 | 3.8 | 13.29 |
| Li ⁺ | 33.63 | 4.22 | 27.62 | 1.95 | 19.28 | 3.84 | 11.5 |
| Sr ⁺² | 33.39 | 4.27 | 27.17 | 2.06 | 19.02 | 3.54 | 12.32 |
| Ca ⁺² | 33.47 | 4.29 | 27.61 | 2.06 | 18.72 | 3.89 | 9.96 |
| Mg ⁺² | 33.25 | 4.58 | 27.41 | 1.50 | 19.32 | 3.76 | 13.29 |

(C) Spectral properties and area ratio: P6C

| Ion | ν_{abs} | Γ_{abs} | ν_{LE} | Γ_{LE}^{inh} | ν_{CT} | Γ_{CT}^{inh} | $\frac{\alpha_{CT}}{\alpha_{LE}}$ |
|------------------|-------------|----------------|------------|---------------------|------------|---------------------|-----------------------------------|
| Na ⁺ | 33.67 | 4.26 | 26.28 | 1.70 | 20.06 | 3.88 | 49.0 |
| Li ⁺ | 33.55 | 4.31 | 26.61 | 2.05 | 19.88 | 3.93 | 43.6 |
| Sr ⁺² | 33.40 | 4.37 | 26.80 | 1.50 | 19.63 | 3.35 | 49.0 |
| Ca ⁺² | 33.45 | 4.38 | 26.80 | 1.50 | 19.28 | 4.19 | 54.6 |
| Mg ⁺² | 33.22 | 4.58 | 25.58 | 1.87 | 20.01 | 3.97 | 49.0 |

^{a)} Peak frequencies (ν) and band widths (Γ , fwhm) are in the unit of 10^3 cm^{-1} . $\frac{\alpha_{CT}}{\alpha_{LE}}$ denotes the ratio of the areas under CT and LE emission bands .

Table S2: LiClO₄ Concentration Dependence of C153 in Ethyl Acetate and Acetonitrile

(A) Spectral properties of C153 in Ethyl Acetate + LiClO₄ Solution ^{a)}

| Conc (M) | n (ref. index) | v _{abs} | Γ _{abs} | v _{em} | Γ _{em} | k _{net} ^{rad} | k _{net} ^{nr} | M _{em} |
|----------|----------------|------------------|------------------|-----------------|-----------------|---------------------------------|--------------------------------|-----------------|
| 0.0 | 1.368 | 24.76 | 4.31 | 19.35 | 3.78 | 1.26 | 7.50 | 4.9 |
| 0.005 | 1.368 | 24.63 | 3.94 | 19.36 | 3.89 | 1.27 | 7.46 | 4.9 |
| 0.01 | 1.368 | 24.63 | 3.99 | 19.29 | 3.94 | 1.27 | 7.80 | 4.9 |
| 0.025 | 1.368 | 24.63 | 4.02 | 19.11 | 4.06 | 1.32 | 8.07 | 5.0 |
| 0.05 | 1.368 | 24.57 | 4.01 | 18.90 | 4.13 | 1.42 | 9.48 | 5.3 |
| 0.075 | 1.368 | 24.55 | 4.00 | 18.76 | 4.18 | 1.37 | 10.30 | 5.3 |
| 0.1 | 1.369 | 24.58 | 4.03 | 18.67 | 4.13 | 1.35 | 10.16 | 5.3 |
| 0.25 | 1.371 | 24.48 | 4.18 | 18.18 | 3.73 | 1.16 | 9.47 | 5.2 |
| 0.5 | 1.374 | 24.31 | 4.36 | 18.11 | 3.59 | 1.15 | 10.15 | 5.1 |
| 0.75 | 1.378 | 24.08 | 4.19 | 18.00 | 3.55 | 1.13 | 10.04 | 5.1 |
| 1.0 | 1.382 | 23.93 | 4.14 | 17.93 | 3.65 | 1.07 | 10.26 | 5.0 |
| 1.5 | 1.387 | 23.62 | 4.16 | 17.82 | 3.65 | 1.06 | 11.05 | 5.0 |
| 2.0 | 1.392 | 23.43 | 4.12 | 17.73 | 3.63 | 1.05 | 11.83 | 5.2 |
| 2.5 | 1.395 | 23.20 | 4.09 | 17.64 | 3.62 | 1.09 | 13.34 | 5.1 |
| 3.0 | 1.395 | 23.12 | 4.19 | 17.56 | 3.58 | 1.00 | 14.85 | 4.8 |

(B) Spectral properties of C153 in Acetonitrile + LiClO₄ Solution

| Conc (M) | n (ref. index) | v _{abs} | Γ _{abs} | v _{em} | Γ _{em} | k _{net} ^{rad} | k _{net} ^{nr} | M _{em} |
|----------|----------------|------------------|------------------|-----------------|-----------------|---------------------------------|--------------------------------|-----------------|
| 0.0 | 1.338 | 24.21 | 4.12 | 18.53 | 3.64 | 1.24 | 5.56 | 5.3 |
| 0.005 | 1.339 | 24.18 | 4.07 | 18.50 | 3.66 | 1.24 | 5.83 | 5.3 |
| 0.01 | 1.339 | 24.38 | 4.42 | 18.45 | 3.67 | 1.23 | 6.04 | 5.3 |
| 0.025 | 1.340 | 24.08 | 4.19 | 18.38 | 3.69 | 1.25 | 6.42 | 5.4 |
| 0.05 | 1.340 | 24.22 | 4.17 | 18.38 | 3.74 | 1.24 | 6.67 | 5.4 |
| 0.075 | 1.341 | 24.34 | 4.63 | 18.24 | 3.65 | 1.22 | 6.87 | 5.4 |
| 0.1 | 1.341 | 24.23 | 4.21 | 18.18 | 3.65 | 1.21 | 7.09 | 5.4 |
| 0.25 | 1.343 | 24.74 | 4.03 | 18.11 | 3.71 | 1.19 | 7.60 | 5.4 |
| 0.5 | 1.346 | 24.28 | 4.50 | 17.99 | 3.63 | 1.17 | 8.16 | 5.4 |
| 0.75 | 1.349 | 23.97 | 4.49 | 17.86 | 3.62 | 1.09 | 9.27 | 5.2 |
| 0.9 | 1.352 | 23.73 | 4.32 | 17.77 | 3.61 | 1.07 | 9.90 | 5.2 |
| 1.0 | 1.353 | 23.83 | 4.88 | 17.72 | 3.59 | 0.92 | 11.29 | 4.9 |

^{a)} Units are same as those in Table S1. M_{em} represents emission transition moment (in Debye unit)

Table S3: Ion Size Dependence of C153 in 0.5(M) Perchlorate Solutions of Ethyl Acetate and Acetonitrile^a

(A) Ethyl Acetate

| Ion | n (ref. index) | v _{abs} | Γ _{abs} | v _{em} | Γ _{em} | k _{net} ^{rad} | k _{net} ^{nr} | M _{em} | Φ |
|------------------|----------------------|------------------|------------------|-----------------|-----------------|---------------------------------|--------------------------------|-----------------|------|
| Na ⁺ | 1.374 | 24.39 | 4.11 | 18.17 | 3.94 | 0.95 | 9.51 | 4.6 | 0.50 |
| Li ⁺ | 1.374 | 24.31 | 4.36 | 18.11 | 3.59 | 1.15 | 10.15 | 5.1 | 0.53 |
| Sr ⁺² | 1.386 | 24.19 | 4.75 | 17.87 | 3.56 | 0.94 | 11.48 | 4.7 | 0.45 |
| Ca ⁺² | 1.382 | 24.08 | 4.29 | 17.72 | 3.54 | 1.02 | 12.43 | 4.9 | 0.45 |
| Mg ⁺² | 1.381 | 24.01 | 5.82 | 18.16 | 3.82 | 0.91 | 13.10 | 4.5 | 0.41 |

(B) Acetonitrile

| Ion | n (ref. index) | v _{abs} | Γ _{abs} | v _{em} | Γ _{em} | k _{net} ^{rad} | k _{net} ^{nr} | M _{em} | Φ |
|------------------|----------------------|------------------|------------------|-----------------|-----------------|---------------------------------|--------------------------------|-----------------|------|
| Na ⁺ | 1.346 | 24.14 | 4.28 | 18.09 | 3.68 | 1.09 | 7.54 | 5.1 | 0.59 |
| Li ⁺ | 1.346 | 24.28 | 4.50 | 17.99 | 3.63 | 1.17 | 8.16 | 5.4 | 0.59 |
| Sr ⁺² | 1.361 | 23.48 | 4.36 | 17.68 | 3.54 | 1.09 | 10.11 | 5.3 | 0.52 |
| Ca ⁺² | 1.356 | 23.37 | 4.04 | 17.58 | 3.48 | 1.20 | 10.25 | 5.6 | 0.54 |
| Mg ⁺² | 1.355 | 22.92 | 4.89 | 17.74 | 3.67 | 1.06 | 11.46 | 5.1 | 0.48 |

^{a)} Units are same as in Tables S1 and S2. Φ represents quantum yield.

Figure Caption

Fig. S1: Fluorescence emission spectra of P5C in several concentrations of LiClO₄ in ethyl acetate (upper panel) and acetonitrile (lower panel). Spectra shown in this figure correspond to the following LiClO₄ concentrations (M) in ethyl acetate and acetonitrile: 0.0, 0.1, 0.25, and 0.5, 1.0, respectively. Note here that we have shown spectra in ethyl acetate with LiClO₄ only upto 1.0 M even though we could go upto 2.5 M.

Fig. S2: Fluorescence emission spectra of P6C in several concentrations of LiClO₄ in ethyl acetate (upper panel) and acetonitrile (lower panel). The spectra shown here correspond to the following LiClO₄ concentrations (M): 0.0, 0.1, 0.25, 0.5, 1.0, respectively. Note that we have shown spectra in ethyl acetate with LiClO₄ only upto 1.0 M even though we could go upto 2.5 M.

Fig. S3: Ion size dependence of change in reaction free energy ($-\Delta G_r$) for LE \rightarrow CT conversion in ethyl acetate (open symbols) and acetonitrile (filled symbols). Note that Mg⁺² has not been shown in this figure. Values (in proper unit) of $-\Delta G_r$ in presence of Mg⁺² in ethyl acetate for P4C, P5C and P6C are respectively -0.82, 6.03, 8.90. Corresponding values in acetonitrile are 2.06, 9.02 and 11.47.

Fig. S4: Upper panel (open symbols) shows the quantum yield for the LE bands and lower panel (filled symbols) for CT bands in EA at different LiClO₄ concentrations. Squares, circles and triangles represent electrolyte concentration dependent quantum

yields of P4C, P5C and P6C, respectively. Estimated errors for these calculations are within $\pm 10\%$ about the average for most of the cases.

Fig. S5: Electrolyte (LiClO_4) concentration dependence of quantum yield (Φ) for C153 in ethyl acetate and acetonitrile. Open circles and open triangles represent quantum yields of C153 in ethyl Acetate and acetonitrile, respectively. Estimated errors for these calculations are within $\pm 10\%$ about the average for most of the cases.

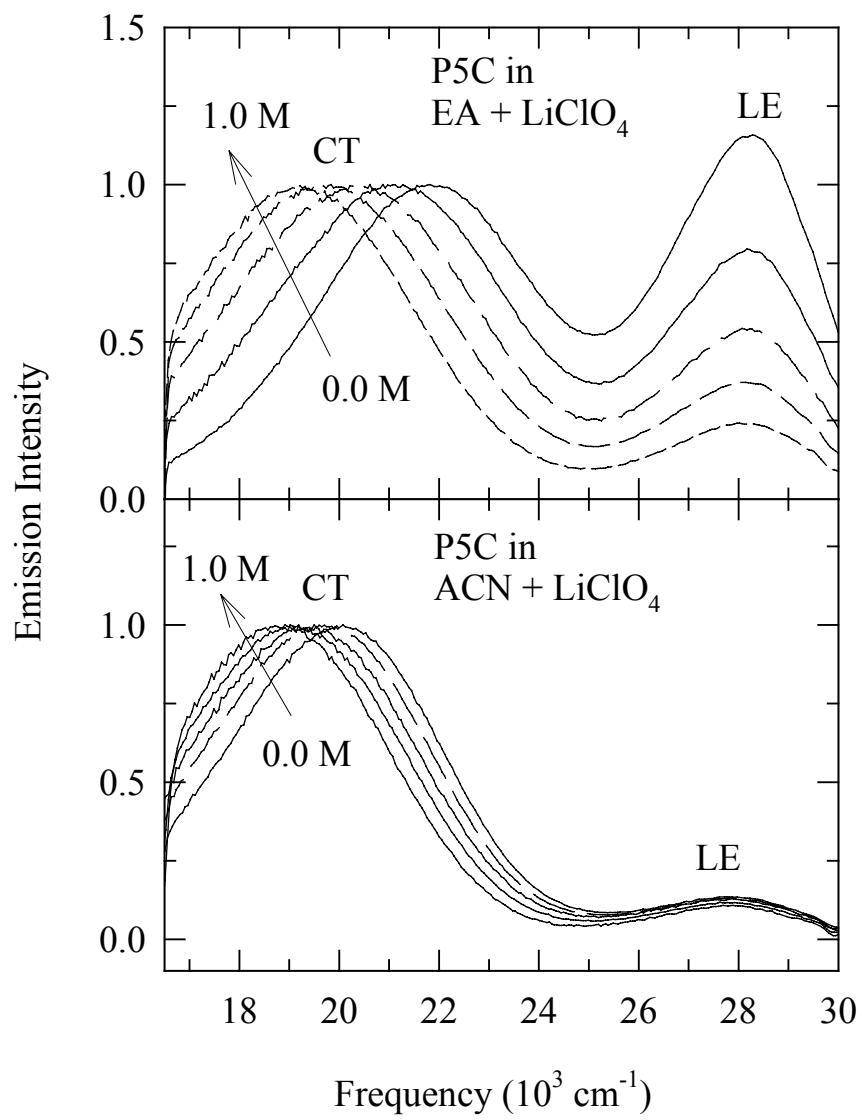


Fig.S1/Pradhan & Biswas

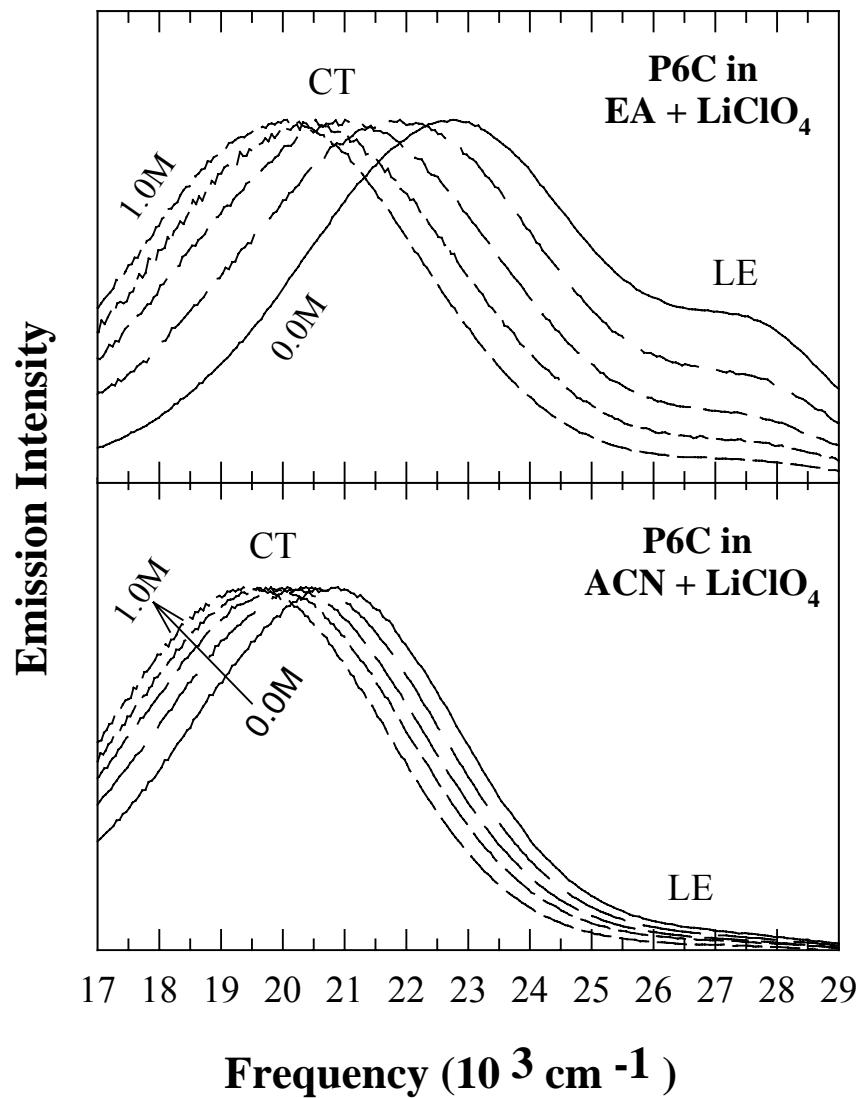


Fig.S2 /Pradhan & Biswas

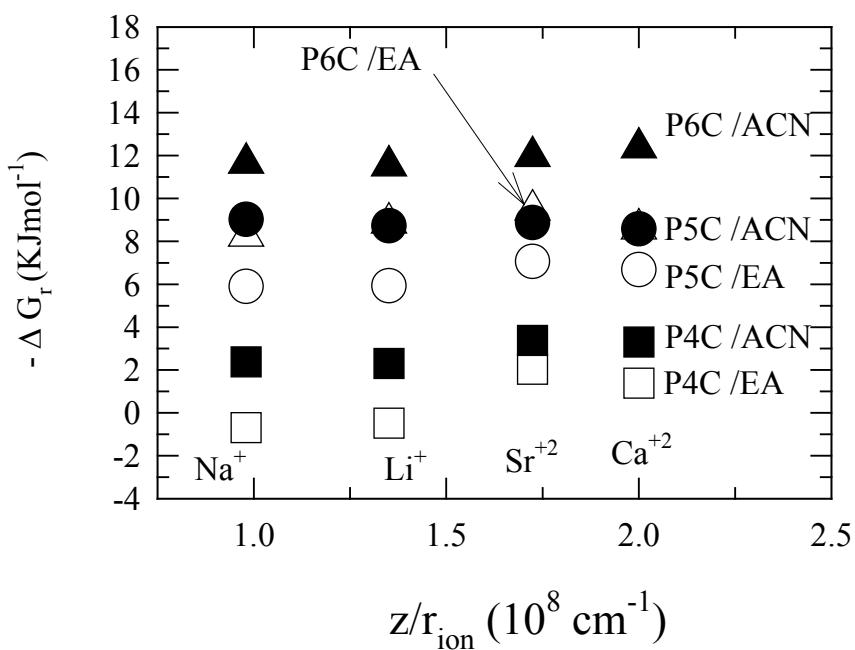


Fig.S3 /Pradhan & Biswas

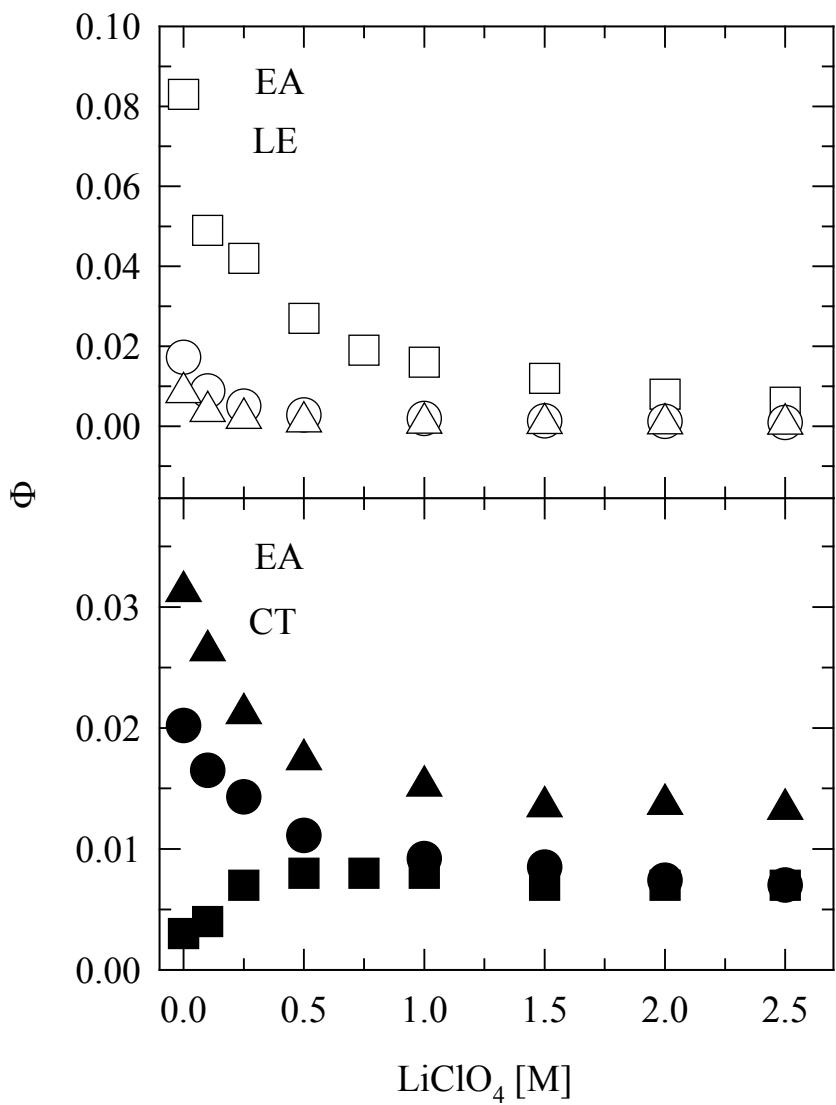


Fig.S4/Pradhan & Biswas

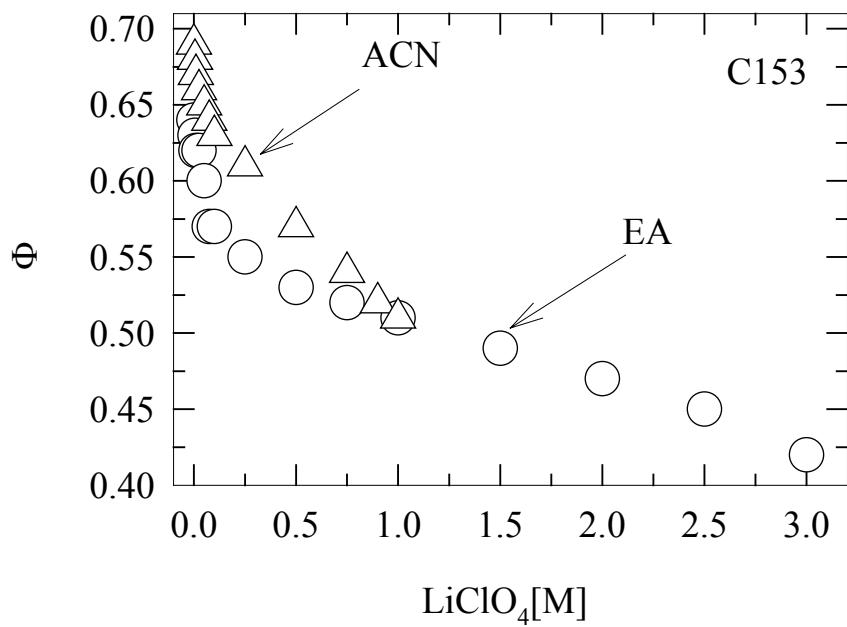


Fig.S5/Pradhan & Biswas