

Supplementary Information for

# An Integrated High-throughput Robotic Platform and Active Learning Approach for Accelerated Discovery of Optimal Electrolyte Formulations

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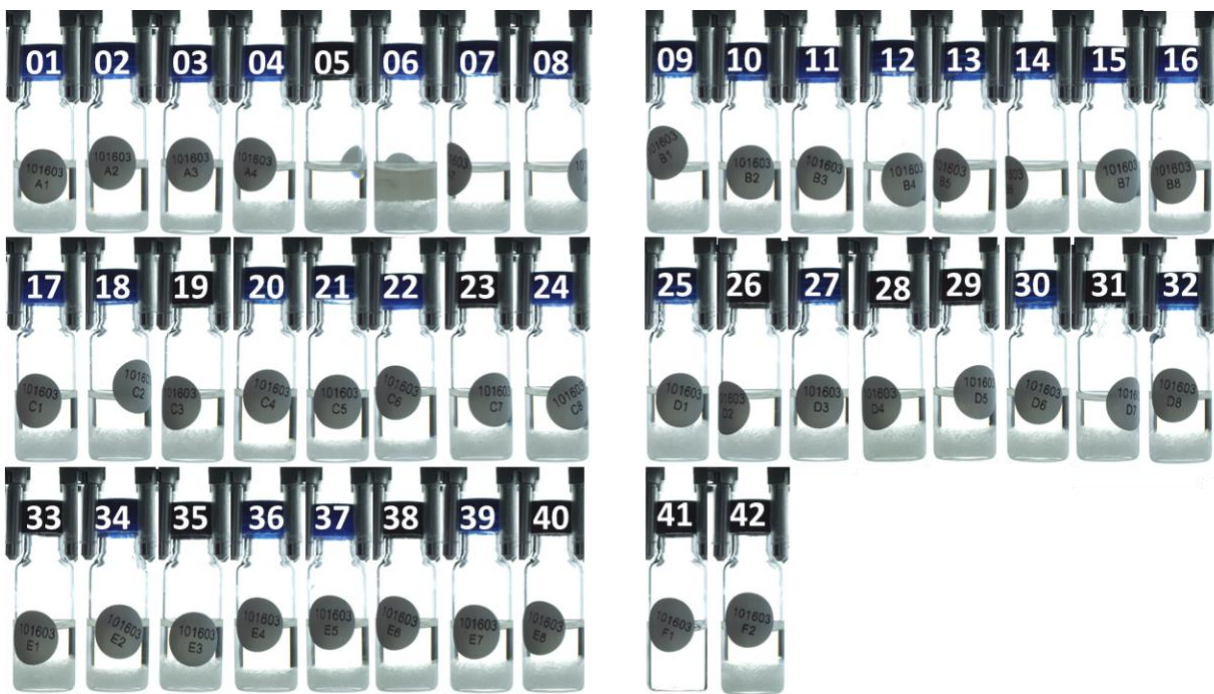
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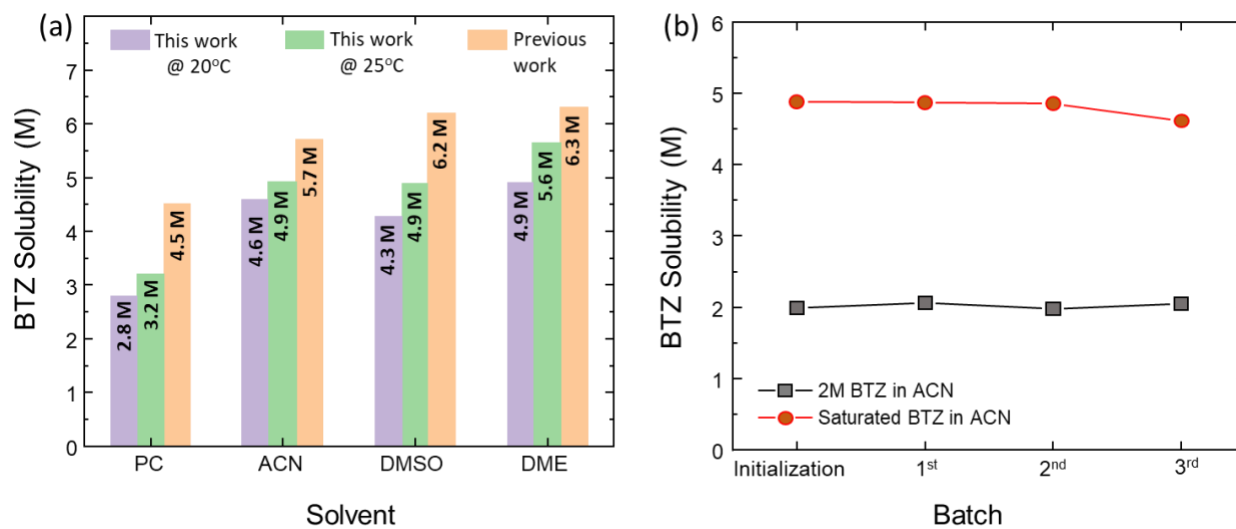
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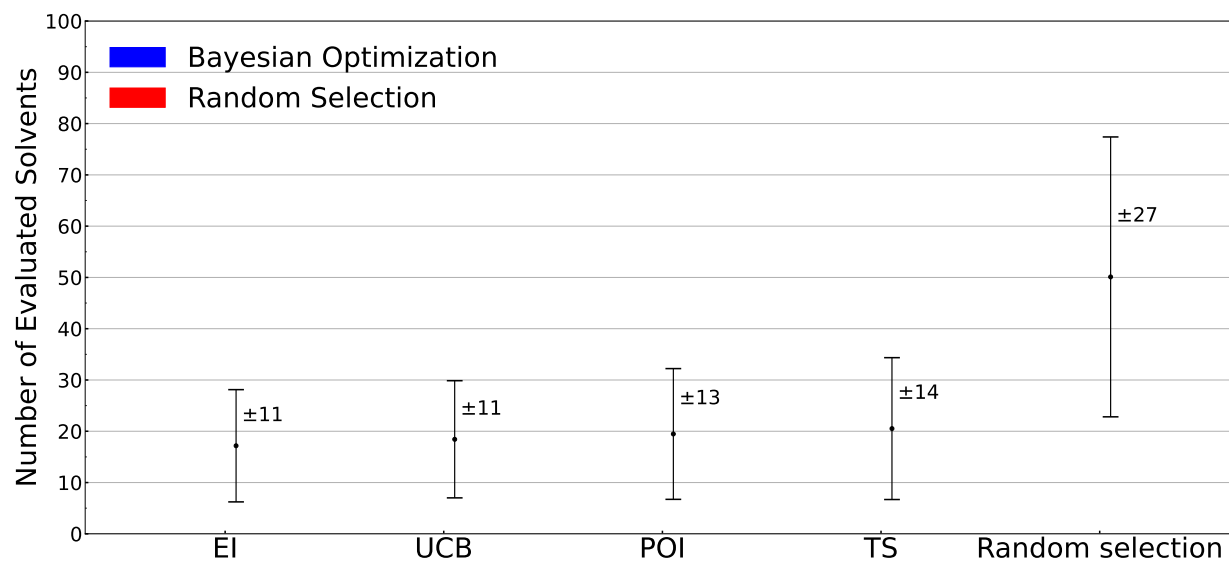
**Fig. S1.** Photograph of our automated HTE robotic platform for sample preparation.



**Fig. S2.** Photograph of saturated solutions prior to solubility measurement.

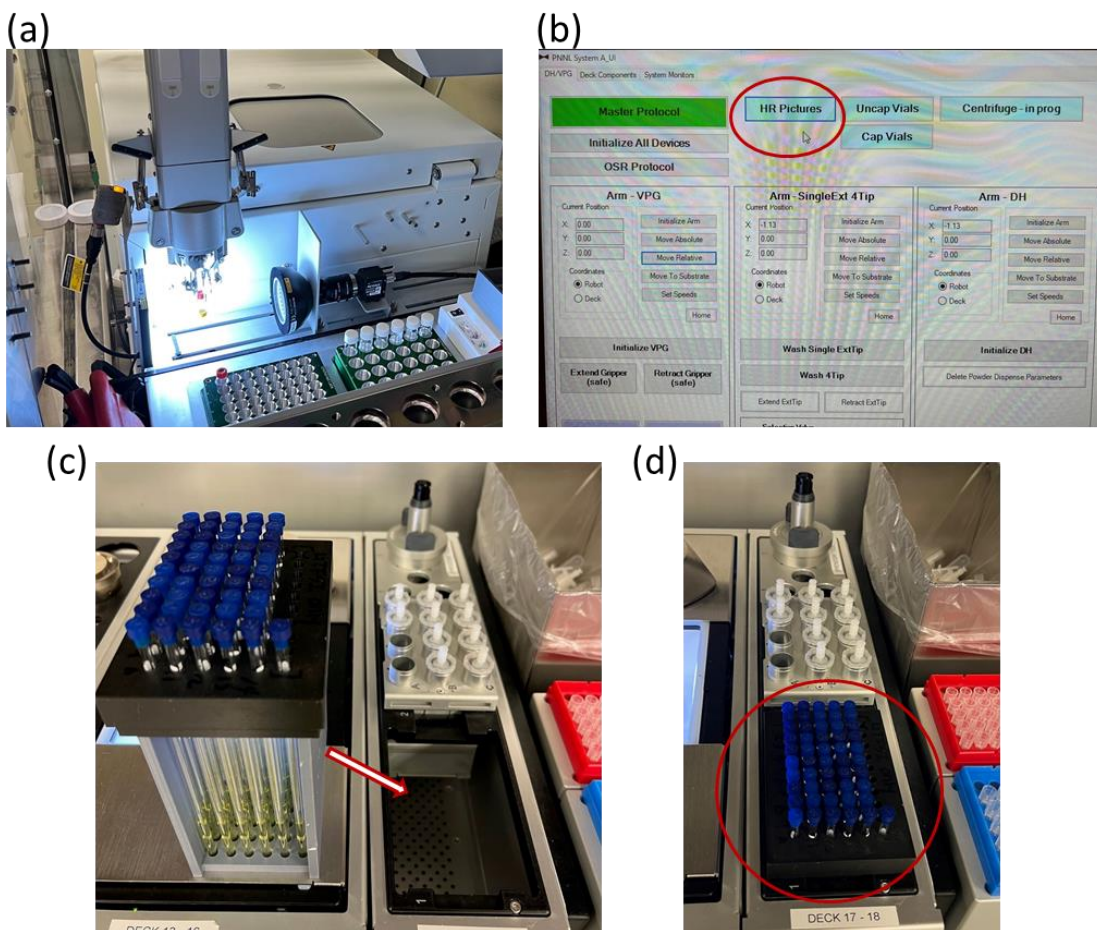


**Fig. S3.** (a) Measured solubilities of BTZ in various solvents in previous (*ACS Energy Letters* 2, 1156-1161 (2017)) and current work. (b) Concentrations of BTZ in two control samples across various batches. Source data are provided as a Source Data file.

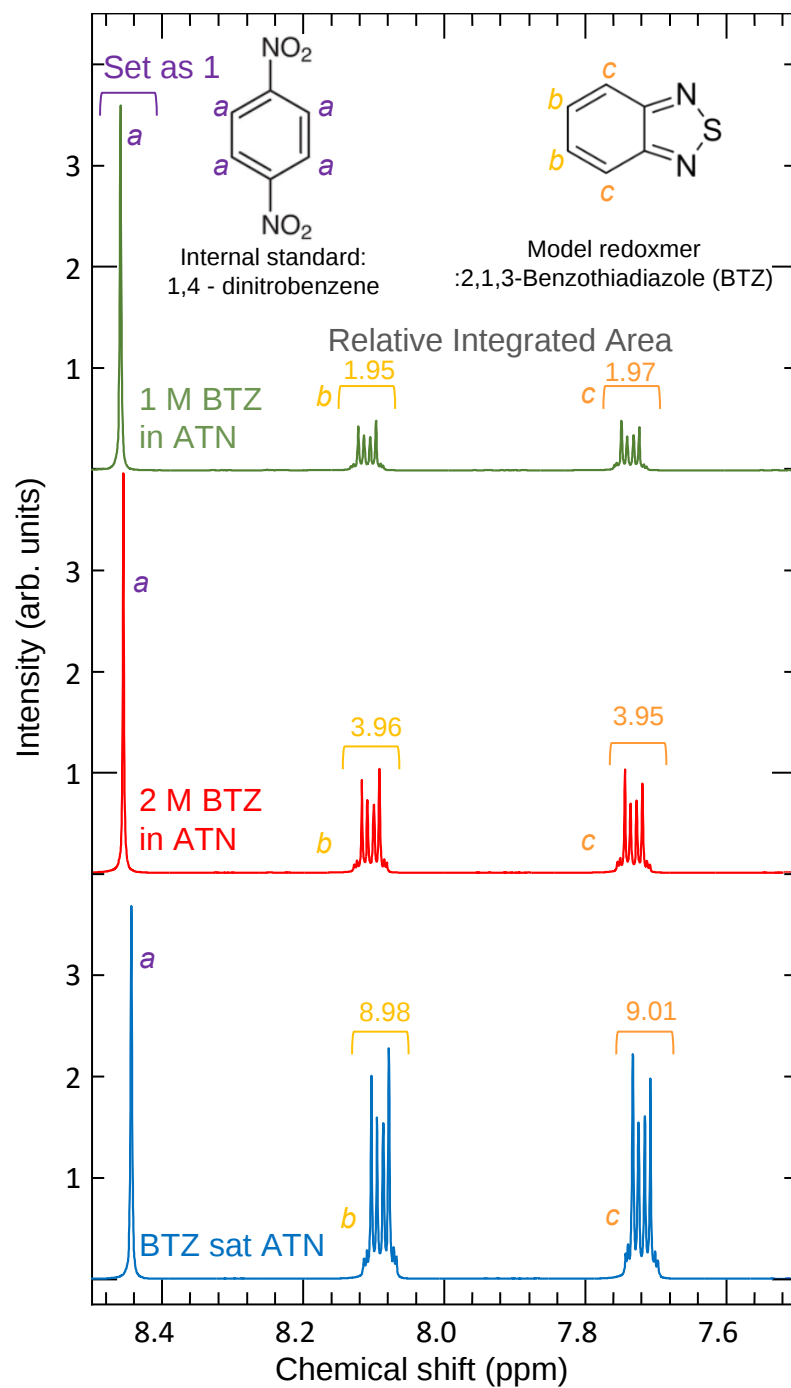


**Fig. S4.** Comparison of random selection versus Bayesian optimization using various acquisitions on the initial known dataset of 98 solvents. The height of the color bar and black error bar represent the mean and standard deviation of 100 trials. EI, UCB, POI, and TS stand for expected improvement, upper confidence bound, probability of improvement, and Thompson sampling. Source data are provided as a Source Data file.

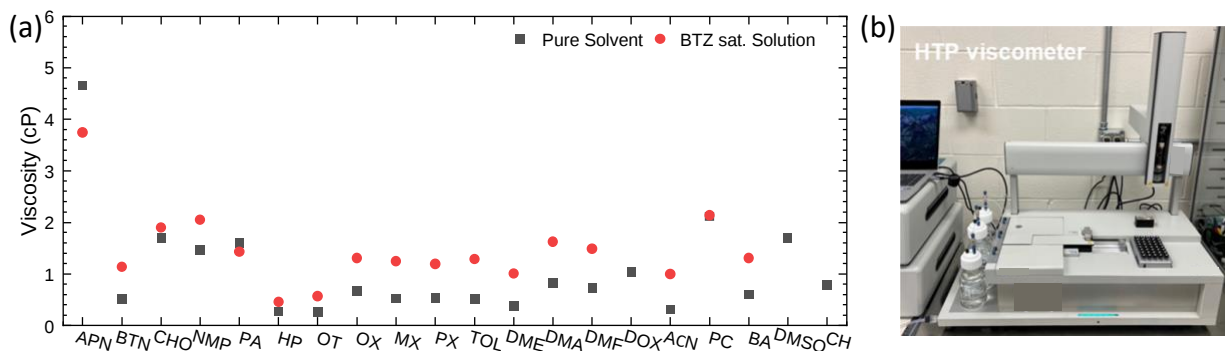




**Fig. S6.** Integration of (a) Keyence's CV-X vision system and (b) its control software in the operating system of our robotic platform. (c) Stand-alone and (d) on-deck picture of the 3D-printed NMR tube holder.



**Fig. S7.** <sup>1</sup>H-NMR spectra of 2,1,3-benzothiadiazole (BTZ) and 1,4-dinitrobenzene (DNB) for concentration quantification and their molecular structures.



**Fig. S8.** (a) Steady shear viscosity as a function of solvent at 20 °C. (b) The high-throughput viscometer (VROC<sup>®</sup> initium one plus, RheoSense) used in this study. Source data are provided as a Source Data file.

**Table. S1.** Summary of processing time for Manual Excess Solute and HTE Excess Solute (this work).

|                                                 |                      | Manual<br>Excess Solute | HTE<br>Excess Solute | Automated<br>Excess Solvent |
|-------------------------------------------------|----------------------|-------------------------|----------------------|-----------------------------|
| Experimental<br>runtime (min)                   | Programing           | 0                       | 30                   |                             |
|                                                 | Solution Preparation | 10                      | 330                  |                             |
|                                                 | Stabilization        | 480                     | 480                  |                             |
|                                                 | NMR Sampling         | 15                      | 120                  |                             |
|                                                 | NMR Measurement      | 15                      | 600                  |                             |
|                                                 | Post-Analysis        | 5                       | 60                   |                             |
|                                                 | Total Process Time   | 525                     | 1620                 |                             |
| Number of samples in a single batch             |                      | 1                       | 42                   |                             |
| Experimental runtime per sample<br>(min/sample) |                      | 525                     | 38.6                 | 20-80*                      |

\*Shiri P, et al. iScience 24, 102176 (2021).

**Table S2.** Measured solubilities of BTZ in 22 single solvents at 20 °C.

| Solvent | Molarity (M, mol/L) |
|---------|---------------------|
| DME     | 4.93                |
| DOX     | 5.47                |
| ACN     | 4.27                |
| DMF     | 5.39                |
| DMA     | 5.21                |
| PC      | 2.79                |
| BA      | 4.17                |
| DMSO    | 4.26                |
| CH      | 2.06                |
| TOL     | 4.79                |
| HP      | 0.96                |
| OT      | 0.97                |
| PA      | 1.57                |
| PX      | 4.40                |
| MX      | 4.49                |
| OX      | 4.57                |
| NMP     | 5.48                |
| CHO     | 5.09                |
| HMPA    | 4.49                |
| BTN     | 4.20                |
| APN     | 2.28                |
| GTN     | 1.86                |

**Table S3.** Measured solubilities of BTZ in 36 binary solvents at 20 °C.

| Solvent 1 | Volume fraction 1 | Solvent 2 | Volume fraction 2 | Molarity (M) |
|-----------|-------------------|-----------|-------------------|--------------|
| DME       | 0.5               | CH        | 0.5               | 4.3          |
| PC        | 0.5               | DMSO      | 0.5               | 3.59         |
| BA        | 0.5               | CH        | 0.5               | 3.7          |
| PC        | 0.5               | BA        | 0.5               | 4.05         |
| DME       | 0.5               | PC        | 0.5               | 4.13         |
| ACN       | 0.5               | DMA       | 0.5               | 4.87         |
| DMA       | 0.5               | PC        | 0.5               | 4.2          |
| ACN       | 0.5               | DMSO      | 0.5               | 4.26         |
| PC        | 0.5               | CH        | 0.5               | 4.28         |
| BA        | 0.5               | DMSO      | 0.5               | 4.76         |
| ACN       | 0.5               | BA        | 0.5               | 4.56         |
| DOX       | 0.5               | CH        | 0.5               | 4.88         |
| DME       | 0.5               | BA        | 0.5               | 4.59         |
| DOX       | 0.5               | PC        | 0.5               | 4.63         |
| DME       | 0.5               | DMSO      | 0.5               | 5.03         |
| DMSO      | 0.5               | CH        | 0.5               | 4.68         |
| ACN       | 0.5               | DMF       | 0.5               | 4.86         |
| DMF       | 0.5               | DMSO      | 0.5               | 4.83         |
| DMA       | 0.5               | CH        | 0.5               | 4.84         |
| ACN       | 0.5               | PC        | 0.5               | 3.43         |
| DMF       | 0.5               | PC        | 0.5               | 4.14         |
| DOX       | 0.5               | BA        | 0.5               | 4.88         |
| DME       | 0.5               | DMF       | 0.5               | 5.4          |
| DMA       | 0.5               | DMSO      | 0.5               | 4.9          |
| ACN       | 0.5               | CH        | 0.5               | 4.64         |
| DOX       | 0.5               | DMA       | 0.5               | 5.59         |
| DMA       | 0.5               | BA        | 0.5               | 5.1          |
| DMF       | 0.5               | CH        | 0.5               | 5.24         |
| ACN       | 0.5               | DOX       | 0.5               | 5.3          |
| DME       | 0.5               | DMA       | 0.5               | 5.3          |
| DOX       | 0.5               | DMSO      | 0.5               | 5.37         |
| DMF       | 0.5               | DMA       | 0.5               | 5.37         |
| ACN       | 0.5               | DME       | 0.5               | 4.58         |
| DME       | 0.5               | DOX       | 0.5               | 5.44         |
| DMF       | 0.5               | BA        | 0.5               | 5.07         |
| DOX       | 0.5               | DMF       | 0.5               | 5.67         |

**Table S4.** List of 11 features used in GPR models and Bayesian optimization workflow

| No. | Feature name                               | Type                                  | Feature creation |
|-----|--------------------------------------------|---------------------------------------|------------------|
| 1   | Topological surface area                   | Solvent, Molecular                    | RDKit            |
| 2   | Molecular weight                           | Solvent, Molecular                    | RDKit            |
| 3   | Number of heavy atoms                      | Solvent, Molecular                    | RDKit            |
| 4   | Octanol/water partition coefficient (logP) | Solvent, Molecular                    | RDKit            |
| 5   | Solvation free energies                    | Solute in continuum model, Electronic | Gaussian 16      |
| 6   | Dipole moment                              | Solute, Electronic                    | Gaussian 16      |
| 7   | Polarizability                             | Solute, Electronic                    | Gaussian 16      |
| 8   | HOMO energy                                | Solute, Electronic                    | Gaussian 16      |
| 9   | LUMO energy                                | Solute, Electronic                    | Gaussian 16      |
| 10  | Maximum partial charge                     | Solute, Electronic                    | Gaussian 16      |
| 11  | Minimum partial charge                     | Solute, Electronic                    | Gaussian 16      |

**Table S5.** Measured solubilities of BTZ in 40 binary solvents at 20 °C (Tested set in Fig. 3a).

| Sample No. | Solvent 1 | Volume fraction 1 | Solvent 2 | Volume fraction 2 | Molarity (M) |
|------------|-----------|-------------------|-----------|-------------------|--------------|
| 046-1      | OT        | 0.4               | HMPA      | 0.6               | 4.31         |
| 046-2      | ACN       | 0.1               | CH        | 0.9               | 3.64         |
| 046-3      | BA        | 0.7               | HP        | 0.3               | 3.81         |
| 046-4      | NMP       | 0.8               | GTN       | 0.2               | 5.37         |
| 046-5      | HP        | 0.3               | CHO       | 0.7               | 4.96         |
| 046-6      | PX        | 0.2               | HMPA      | 0.8               | 5.24         |
| 046-7      | CH        | 0.9               | HP        | 0.1               | 2.07         |
| 046-8      | ACN       | 0.3               | CH        | 0.7               | 5.09         |
| 046-9      | OT        | 0.6               | HMPA      | 0.4               | 3.82         |
| 046-10     | DOX       | 0.6               | DMF       | 0.4               | 6.25         |
| 046-11     | BA        | 0.8               | PX        | 0.2               | 4.61         |
| 046-12     | OT        | 0.7               | HMPA      | 0.3               | 0.00         |
| 046-13     | PX        | 0.1               | HMPA      | 0.9               | 5.23         |
| 046-14     | BA        | 0.1               | OT        | 0.9               | 1.52         |
| 046-15     | HP        | 0.2               | OX        | 0.8               | 4.47         |
| 046-16     | HMPA      | 0.4               | APN       | 0.6               | 3.47         |
| 046-17     | CHO       | 0.6               | HMPA      | 0.4               | 5.54         |
| 046-18     | DMA       | 0.2               | HMPA      | 0.8               | 5.31         |
| 046-19     | DME       | 0.8               | OT        | 0.2               | 5.51         |
| 046-20     | DME       | 0.7               | OX        | 0.3               | 5.99         |
| 046-21     | BA        | 0.7               | APN       | 0.3               | 4.38         |
| 046-22     | DMSO      | 0.1               | HMPA      | 0.9               | 5.16         |
| 046-23     | CH        | 0.9               | PA        | 0.1               | 3.31         |
| 046-24     | HMPA      | 0.7               | APN       | 0.3               | 4.35         |
| 046-25     | OT        | 0.3               | HMPA      | 0.7               | 4.62         |
| 046-26     | OT        | 0.5               | HMPA      | 0.5               | 3.98         |
| 046-27     | ACN       | 0.4               | GTN       | 0.6               | 2.89         |
| 046-28     | DME       | 0.3               | HMPA      | 0.7               | 5.23         |
| 046-29     | DMF       | 0.2               | DMA       | 0.8               | 5.95         |
| 046-30     | HMPA      | 0.4               | BTN       | 0.6               | 4.94         |
| 046-31     | ACN       | 0.4               | HP        | 0.6               | 4.71         |
| 046-32     | OT        | 0.5               | PA        | 0.5               | 2.23         |
| 046-33     | DOX       | 0.2               | OX        | 0.8               | 5.48         |
| 046-34     | ACN       | 0.7               | CH        | 0.3               | 5.61         |
| 046-35     | DOX       | 0.8               | APN       | 0.2               | 6.21         |
| 046-36     | DME       | 0.1               | HMPA      | 0.9               | 5.47         |
| 046-37     | PX        | 0.6               | APN       | 0.4               | 4.57         |
| 046-38     | OT        | 0.8               | HMPA      | 0.2               | 2.78         |

|        |     |     |      |     |      |
|--------|-----|-----|------|-----|------|
| 046-39 | ACN | 0.3 | OT   | 0.7 | 4.13 |
| 046-40 | TOL | 0.5 | HMPA | 0.5 | 5.24 |

**Table S6.** List of BO-suggested solvents and their measured solubilities in the 1<sup>st</sup> batch at 20 °C.

| Sample No. | Solvent 1 | Volume fraction 1 | Solvent 2 | Volume fraction 2 | Molarity (M) |
|------------|-----------|-------------------|-----------|-------------------|--------------|
| 326-01     | DME       | 0.1               | DOX       | 0.9               | 6.07         |
| 326-02     | DOX       | 0.9               | HMPA      | 0.1               | 6.12         |
| 326-03     | DME       | 0.2               | DOX       | 0.8               | 6.01         |
| 326-04     | DME       | 0.3               | DOX       | 0.7               | 5.98         |
| 326-05     | DOX       | 0.9               | BA        | 0.1               | 5.90         |
| 326-06     | DOX       | 0.8               | HMPA      | 0.2               | 5.97         |
| 326-07     | DOX       | 0.9               | DMF       | 0.1               | 5.94         |
| 326-08     | DOX       | 0.9               | NMP       | 0.1               | 6.09         |
| 326-09     | DOX       | 0.9               | DMA       | 0.1               | 5.49         |
| 326-10     | DME       | 0.4               | DOX       | 0.6               | 5.87         |
| 326-11     | DOX       | 0.9               | OX        | 0.1               | 6.30         |
| 326-12     | DOX       | 0.7               | HMPA      | 0.3               | 5.66         |
| 326-13     | DOX       | 0.9               | MX        | 0.1               | 6.08         |
| 326-14     | DOX       | 0.9               | PX        | 0.1               | 6.19         |
| 326-15     | DOX       | 0.9               | DMSO      | 0.1               | 5.58         |
| 326-16     | DOX       | 0.9               | TOL       | 0.1               | 5.90         |
| 326-17     | DME       | 0.5               | DOX       | 0.5               | 5.70         |
| 326-18     | DOX       | 0.8               | BA        | 0.2               | 5.89         |
| 326-19     | DOX       | 0.9               | CHO       | 0.1               | 6.12         |
| 326-20     | DOX       | 0.9               | OT        | 0.1               | 5.74         |
| 326-21     | DOX       | 0.9               | PA        | 0.1               | 6.21         |
| 326-22     | DME       | 0.6               | DOX       | 0.4               | 5.81         |
| 326-23     | DOX       | 0.8               | DMF       | 0.2               | 6.10         |
| 326-24     | DOX       | 0.9               | PC        | 0.1               | 5.45         |
| 326-25     | DOX       | 0.8               | NMP       | 0.2               | 6.34         |
| 326-26     | DOX       | 0.9               | HP        | 0.1               | 6.03         |
| 326-27     | DOX       | 0.6               | HMPA      | 0.4               | 5.56         |
| 326-28     | DOX       | 0.9               | CH        | 0.1               | 6.01         |
| 326-29     | DOX       | 0.8               | DMA       | 0.2               | 5.99         |
| 326-30     | DOX       | 0.7               | BA        | 0.3               | 5.96         |
| 326-31     | DME       | 0.7               | DOX       | 0.3               | 5.82         |
| 326-32     | DOX       | 0.9               | APN       | 0.1               | 5.42         |
| 326-33     | DOX       | 0.8               | OX        | 0.2               | 6.14         |
| 326-34     | DOX       | 0.9               | GTN       | 0.1               | 6.48         |

|        |     |     |      |     |      |
|--------|-----|-----|------|-----|------|
| 326-35 | DOX | 0.8 | DMSO | 0.2 | 6.50 |
| 326-36 | DOX | 0.9 | BTN  | 0.1 | 4.53 |
| 326-37 | DOX | 0.8 | MX   | 0.2 | 6.07 |
| 326-38 | DOX | 0.8 | PX   | 0.2 | 6.03 |
| 326-39 | DOX | 0.5 | HMPA | 0.5 | 5.69 |
| 326-40 | DOX | 0.8 | TOL  | 0.2 | 6.45 |

**Table S7.** List of BO-suggested solvents and their measured solubilities in the 2<sup>nd</sup> batch at 20 °C.

| Sample No. | Solvent 1 | Volume fraction 1 | Solvent 2 | Volume fraction 2 | Molarity (M) |
|------------|-----------|-------------------|-----------|-------------------|--------------|
| 337-01     | DOX       | 0.4               | BA        | 0.6               | 5.66         |
| 337-02     | DOX       | 0.5               | BA        | 0.5               | 5.78         |
| 337-03     | DOX       | 0.3               | NMP       | 0.7               | 6.38         |
| 337-04     | DOX       | 0.4               | NMP       | 0.6               | 6.38         |
| 337-05     | DOX       | 0.3               | BA        | 0.7               | 5.55         |
| 337-06     | DOX       | 0.2               | NMP       | 0.8               | 5.98         |
| 337-07     | DOX       | 0.5               | NMP       | 0.5               | 6.37         |
| 337-08     | DOX       | 0.6               | CHO       | 0.4               | 6.11         |
| 337-09     | DOX       | 0.4               | OX        | 0.6               | 5.94         |
| 337-10     | DOX       | 0.5               | OX        | 0.5               | 5.97         |
| 337-11     | DOX       | 0.5               | CHO       | 0.5               | 6.34         |
| 337-12     | DOX       | 0.3               | DMA       | 0.7               | 6.00         |
| 337-13     | DOX       | 0.4               | MX        | 0.6               | 5.87         |
| 337-14     | DOX       | 0.4               | PX        | 0.6               | 5.90         |
| 337-15     | DMF       | 0.6               | HMPA      | 0.4               | 5.65         |
| 337-16     | DOX       | 0.4               | DMA       | 0.6               | 6.16         |
| 337-17     | DME       | 0.8               | DOX       | 0.2               | 5.87         |
| 337-18     | DOX       | 0.6               | APN       | 0.4               | 5.43         |
| 337-19     | DOX       | 0.5               | PC        | 0.5               | 5.38         |
| 337-20     | DOX       | 0.5               | MX        | 0.5               | 5.94         |
| 337-21     | DOX       | 0.5               | PX        | 0.5               | 5.89         |
| 337-22     | DMF       | 0.5               | HMPA      | 0.5               | 5.06         |
| 337-23     | DOX       | 0.5               | APN       | 0.5               | 4.96         |
| 337-24     | DOX       | 0.6               | GTN       | 0.4               | 5.34         |
| 337-25     | DMF       | 0.7               | HMPA      | 0.3               | 5.67         |
| 337-26     | DOX       | 0.6               | BA        | 0.4               | 5.92         |
| 337-27     | DME       | 0.7               | HMPA      | 0.3               | 5.70         |
| 337-28     | DOX       | 0.5               | GTN       | 0.5               | 4.86         |
| 337-29     | DOX       | 0.2               | DMA       | 0.8               | 6.13         |
| 337-30     | DOX       | 0.4               | PC        | 0.6               | 4.93         |

|        |     |     |      |     |      |
|--------|-----|-----|------|-----|------|
| 337-31 | DME | 0.6 | HMPA | 0.4 | 5.66 |
| 337-32 | DOX | 0.3 | HMPA | 0.7 | 5.79 |
| 337-33 | DOX | 0.6 | PC   | 0.4 | 5.65 |
| 337-34 | DOX | 0.5 | DMA  | 0.5 | 6.45 |
| 337-35 | DME | 0.8 | HMPA | 0.2 | 5.84 |
| 337-36 | DOX | 0.2 | BA   | 0.8 | 5.34 |
| 337-37 | DME | 0.9 | DOX  | 0.1 | 6.40 |
| 337-38 | DME | 0.4 | NMP  | 0.6 | 6.35 |
| 337-39 | DME | 0.4 | DMF  | 0.6 | 6.16 |
| 337-40 | DOX | 0.6 | NMP  | 0.4 | 6.27 |

**Table S8.** List of BO-suggested solvents and their measured solubilities in the 3<sup>rd</sup> batch at 20 °C.

| Sample No. | Solvent 1 | Volume fraction 1 | Solvent 2 | Volume fraction 2 | Molarity (M) |
|------------|-----------|-------------------|-----------|-------------------|--------------|
| 603-01     | DME       | 0.7               | OX        | 0.3               | 5.72         |
| 603-02     | DOX       | 0.6               | DMSO      | 0.4               | 5.97         |
| 603-03     | DOX       | 0.7               | ACN       | 0.3               | 5.92         |
| 603-04     | DME       | 0.7               | PX        | 0.3               | 5.36         |
| 603-05     | DME       | 0.7               | MX        | 0.3               | 5.44         |
| 603-06     | DME       | 0.8               | OX        | 0.2               | 5.60         |
| 603-07     | DME       | 0.8               | MX        | 0.2               | 5.43         |
| 603-08     | DME       | 0.6               | OX        | 0.4               | 5.54         |
| 603-09     | DME       | 0.8               | PX        | 0.2               | 5.64         |
| 603-10     | DME       | 0.8               | TOL       | 0.2               | 5.53         |
| 603-11     | DOX       | 0.5               | DMSO      | 0.5               | 6.10         |
| 603-12     | DME       | 0.9               | TOL       | 0.1               | 5.66         |
| 603-13     | DOX       | 0.5               | DMF       | 0.5               | 6.26         |
| 603-14     | DME       | 0.6               | MX        | 0.4               | 5.32         |
| 603-15     | DME       | 0.6               | PX        | 0.4               | 5.28         |
| 603-16     | DOX       | 0.4               | DMF       | 0.6               | 5.98         |
| 603-17     | DME       | 0.9               | MX        | 0.1               | 5.46         |
| 603-18     | DME       | 0.9               | PX        | 0.1               | 5.05         |
| 603-19     | DME       | 0.9               | OX        | 0.1               | 5.08         |
| 603-20     | DOX       | 0.8               | ACN       | 0.2               | 6.20         |
| 603-21     | DOX       | 0.7               | DMSO      | 0.3               | 6.02         |
| 603-22     | DOX       | 0.6               | ACN       | 0.4               | 6.04         |
| 603-23     | DME       | 0.7               | TOL       | 0.3               | 5.31         |
| 603-24     | DOX       | 0.6               | PA        | 0.4               | 5.61         |
| 603-25     | DME       | 0.9               | DMSO      | 0.1               | 5.67         |

|        |     |     |      |     |      |
|--------|-----|-----|------|-----|------|
| 603-26 | DME | 0.9 | CH   | 0.1 | 5.65 |
| 603-27 | DME | 0.9 | HP   | 0.1 | 5.53 |
| 603-28 | DME | 0.9 | OT   | 0.1 | 5.21 |
| 603-29 | DME | 0.8 | DMSO | 0.2 | 5.74 |
| 603-30 | DME | 0.8 | DMF  | 0.2 | 5.85 |
| 603-31 | DME | 0.9 | DMF  | 0.1 | 5.77 |
| 603-32 | DME | 0.7 | DMF  | 0.3 | 5.80 |
| 603-33 | DOX | 0.5 | PA   | 0.5 | 5.46 |
| 603-34 | DOX | 0.3 | DMF  | 0.7 | 6.14 |
| 603-35 | DME | 0.9 | DMA  | 0.1 | 5.71 |
| 603-36 | DOX | 0.4 | DMSO | 0.6 | 5.88 |
| 603-37 | DOX | 0.7 | PA   | 0.3 | 6.14 |
| 603-38 | DME | 0.6 | DMF  | 0.4 | 5.95 |
| 603-39 | DME | 0.8 | DMA  | 0.2 | 5.74 |
| 603-40 | DME | 0.9 | NMP  | 0.1 | 5.86 |

**Table S9.** Stabilization time comparison after mixing the solutions.

| Solvent | Molarity (M, mol/L at 20 °C) |         |          |
|---------|------------------------------|---------|----------|
|         | 6 hours                      | 8 hours | 20 hours |
| DOX     | 5.50                         | 5.47    | 5.48     |
| PC      | 2.77                         | 2.79    | 2.78     |
| DMSO    | 4.30                         | 4.26    | 4.31     |
| CH      | 2.08                         | 2.06    | 2.09     |
| ACN     | 4.77                         | 4.64    | 4.8      |